

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 02 May 2001 (02.05.01)	
International application No. PCT/JP00/05229	Applicant's or agent's file reference 662024
International filing date (day/month/year) 04 August 2000 (04.08.00)	Priority date (day/month/year) 05 August 1999 (05.08.99)
Applicant HIBI, Takuo et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 29 January 2001 (29.01.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer R. Forax Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 662024	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/JP 00/ 05229	International filing date (day/month/year) 04/08/2000	(Earliest) Priority Date (day/month/year) 05/08/1999
Applicant SUMITOMO CHEMICAL COMPANY LIMITED		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

P 00/05229

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/46 C01B7/04 B01J21/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	EP 0 936 184 A (SUMITOMO CHEMICAL CO) 18 August 1999 (1999-08-18) claims 1,26,27 page 27, line 44 - line 47 ---	1-5,8-10
Y	EP 0 389 041 A (SHELL INT RESEARCH) 26 September 1990 (1990-09-26) claims 1,12,13 ---	1-5,8-10
A	US 4 847 231 A (THAMPI KRISHNAN R ET AL) 11 July 1989 (1989-07-11) claims 1,15 ---	
A	FR 2 765 120 A (RHONE POULENC CHIMIE) 31 December 1998 (1998-12-31) claims 1,3 --- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

21 November 2000

Date of mailing of the international search report

28/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Thion, M

INTERNATIONAL SEARCH REPORT

International Application No

JP 00/05229

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 126 552 A (TOA NENRYO KOGYO KK) 28 November 1984 (1984-11-28) page 3, line 31 - line 34 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 00/05229

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0936184	A	18-08-1999	CN 1245773 A SG 71193 A	01-03-2000 21-03-2000
EP 0389041	A	26-09-1990	AT 96053 T AU 627004 B AU 5211790 A BR 9001319 A CA 2012663 A CN 1045763 A, B DE 69003978 D DE 69003978 T DK 389041 T ES 2045751 T GR 3026117 T IE 63314 B JP 2284650 A NO 301068 B NZ 233026 A RU 2007216 C US 5106549 A ZA 9002169 A	15-11-1993 13-08-1992 27-09-1990 02-04-1991 23-09-1990 03-10-1990 25-11-1993 10-02-1994 15-11-1993 16-01-1994 29-05-1998 05-04-1995 22-11-1990 08-09-1997 27-08-1991 15-02-1994 21-04-1992 28-12-1990
US 4847231	A	11-07-1989	NONE	
FR 2765120	A	31-12-1998	NONE	
EP 0126552	A	28-11-1984	JP 1025731 B JP 1540629 C JP 59204145 A CA 1216002 A DE 3467752 D US 4551556 A	19-05-1989 31-01-1990 19-11-1984 30-12-1986 07-01-1988 05-11-1985

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)



To:

AOYAMA, Tamotsu
Aoyama & Partners
IMP Building
3-7, Shiromi 1-chome, Chuo-ku
Osaka-shi, Osaka 540-0001
JAPON

Date of mailing (day/month/year) 08 December 2000 (08.12.00)	
Applicant's or agent's file reference 662024	IMPORTANT NOTIFICATION
International application No. PCT/JP00/05229	International filing date (day/month/year) 04 August 2000 (04.08.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 05 August 1999 (05.08.99)
Applicant SUMITOMO CHEMICAL COMPANY, LIMITED et al	

- The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
05 Augu 1999 (05.08.99)	11/222292	JP	12 Sept 2000 (12.09.00)
05 Augu 1999 (05.08.99)	11/222293	JP	12 Sept 2000 (12.09.00)
05 Apri 2000 (05.04.00)	2000/103202	JP	12 Sept 2000 (12.09.00)
14 June 2000 (14.06.00)	2000/178003	JP	12 Sept 2000 (12.09.00)
07 July 2000 (07.07.00)	2000/206304	JP	12 Sept 2000 (12.09.00)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Masashi HONDA

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

AOYAMA, Tamotsu
Aoyama & Partners
IMP Building
3-7, Shiromi 1-chome, Chuo-ku
Osaka-shi, Osaka 540-0001
JAPON



Date of mailing (day/month/year) 15 February 2001 (15.02.01)		
Applicant's or agent's file reference 662024		IMPORTANT NOTICE
International application No. PCT/JP00/05229	International filing date (day/month/year) 04 August 2000 (04.08.00)	Priority date (day/month/year) 05 August 1999 (05.08.99)
Applicant SUMITOMO CHEMICAL COMPANY, LIMITED et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
AU, KR, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
AE, AG, AL, AM, AP, AT, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EA, EE, EP, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OA, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA,
The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).
3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
15 February 2001 (15.02.01) under No. WO 01/10550

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

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15From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:
AOYAMA, Tamotsu
AOYAMA & PARTNERS
IMP Building, 3-7,
Shiromi 1-chome, Chuo-ku,
Osaka-shi, Osaka 540-0001
JAPON

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)Date of mailing
(day/month/year) 31.10.2001Applicant's or agent's file reference
662024

IMPORTANT NOTIFICATION

International application No.
PCT/JP00/05229International filing date (day/month/year)
04/08/2000Priority date (day/month/year)
05/08/1999Applicant
SUMITOMO CHEMICAL COMPANY LIMITED

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Ferro Vasconcelos, M

Tel. +49 89 2399-7995




PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 662024	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/JP00/05229	International filing date (day/month/year) 04/08/2000	Priority date (day/month/year) 05/08/1999	
International Patent Classification (IPC) or national classification and IPC B01J23/46			
Applicant SUMITOMO CHEMICAL COMPANY LIMITED			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input checked="" type="checkbox"/> Lack of unity of invention V <input type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input checked="" type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 			
Date of submission of the demand 29/01/2001		Date of completion of this report 31.10.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Thomasson, P Telephone No. +49 89 2399 8339	



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/JP00/05229

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*):
Description, pages:

1-196 as originally filed

Claims, No.:

1-12 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/JP00/05229

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☒ the entire international application.
- ☐ claims Nos. .

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):
- ☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
see separate sheet
- ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
- ☐ no international search report has been established for the said claims Nos. .

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

- ☐ the written form has not been furnished or does not comply with the standard.
- ☐ the computer readable form has not been furnished or does not comply with the standard.

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.
- ☐ paid additional fees.
- ☐ paid additional fees under protest.
- ☐ neither restricted nor paid additional fees.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/JP00/05229

2. ☒ This Authority found that the requirement of unity of invention is not complied and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
- ☐ complied with.
- ☒ not complied with for the following reasons:
see separate sheet
4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:
- ☒ all parts.
- ☐ the parts relating to claims Nos. .

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP00/05229

Re Item III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The question whether the subject-matter of claims 1-12 appears to be novel, to involve an inventive step or to be industrially applicable has not been examined because the subject-matter of claims 1-12 lacks clarity (see **Re Item VIII**).

Re Item IV

Lack of unity of invention

The present application does not meet the requirement of Unity of invention (Rule 13.1 PCT) for the following reasons:

The separate inventions are:

1. (1) a supported ruthenium catalyst calcined by 550°C (claim 1, (1)),
(2) a supported ruthenium catalyst with a CO_{ads} of at least 87.5 ml/g (claim 1, (2)),
(3) a supported ruthenium catalyst calcined and treated in different atmospheres (claim 1, (3)).

The single general concept linking these different subject-matters is "a supported ruthenium oxide catalyst", which is obviously not inventive.

2. (1) a process for producing a supported ruthenium catalyst according to claim 4, (1),
(2) a process for producing a supported ruthenium catalyst according to claim 4, (2),
(3) a process for producing a supported ruthenium catalyst according to claim 4, (3),
(4) a process for producing a supported ruthenium catalyst according to claim 4, (4),
(5) a process for producing a supported ruthenium catalyst according to claim 4, (5),
(6) a process for producing a supported ruthenium catalyst according to claim 4, (6).

The single general concept linking these different inventions is "a process for producing a supported ruthenium catalyst", which is obviously not inventive.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP00/05229

3. (1) a process for producing chlorine according to claim 8, (1),
(2) a process for producing chlorine according to claim 8, (2),
(3) a process for producing chlorine according to claim 8, (3),
(4) a process for producing chlorine according to claim 8, (4),
(5) a process for producing chlorine according to claim 8, (5),
(6) a process for producing chlorine according to claim 8, (6).

The single general concept linking these different inventions is "a process for producing chlorine", which is obviously not inventive.

Re Item VI

Certain documents cited

Certain published documents (Rule 70.10)

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
EP-A-0 936 184	18/08/1999	16/02/1999	

Re Item VIII

Certain observations on the international application

The present application does not meet the requirements of Article 6 PCT for the following reasons:

1. Claims 1, 4 and 8 indicates a group of respectively 3, 6 and 6 different subject-matters (see **Re Item IV** §1, §2 and §3) and therefore lack conciseness and clarity since the plurality of these subject-matters makes it difficult, if not impossible, to determine the matter for which protection is sought, and places an undue burden on others seeking to establish the extent of the protection.
2. The attention of the applicant is drawn to the fact that characterisation of a product by its parameters should only be allowed in those cases where the invention cannot be adequately defined in any other way. In the case of catalysts, such products can

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP00/05229

be characterized by their chemical composition, by their specific surface areas or in some cases by using product-by-process claims. In the present case, the **carbon monoxide adsorption amount** (see claims 1(2), 4(2) and 8(2)), the **EXAFS-Peak intensities** (claims 4(4) and 8(4)), the **chlorine formation activity** (see claims 4(4), 6, 7, 8(4), 11 and 12) are considered to be some "unusual" parameters (see PCT Gazette, 29/10/1998, "PCT International Preliminary Examination Guidelines", Section IV, III-4.7a) which do not allow any **meaningful comparison with the prior art**. Consequently the said claims lack clarity.

3. Claim 1, which is a **product** claim, indicates some technical features corresponding to a **process** for producing a catalyst (see claim 1(3)). Therefore the category of claim 1 is not clear, so that claim 1 lacks clarity.

DESCRIPTION

SUPPORTED RUTHENIUM OXIDE CATALYST, PROCESS FOR PREPARING
SUPPORTED RUTHENIUM CATALYST AND PROCESS FOR PRODUCING
CHLORINE

5

FIELD OF THE INVENTION

The present invention relates to a supported ruthenium
oxide catalyst, a process for preparing a supported
ruthenium oxide catalyst or a supported ruthenium chloride
10 catalyst, and process for producing chlorine. More
particularly, the present invention relates to a supported
ruthenium oxide catalyst which has a high catalytic
activity and thus produces purpose substance in a smaller
amount at a lower temperature, and which is less sintered
15 during the reaction, simplifies the production steps, and
suffers less deactivation, a process for preparing a
supported ruthenium oxide catalyst or a supported ruthenium
chloride catalyst which have the same characteristics as
above, and a process for producing chlorine by oxidizing
20 hydrogen chloride with oxygen in the presence of such a
catalyst.

PRIOR ART

Firstly, a supported ruthenium oxide catalyst is
explained. The supported ruthenium oxide catalyst is
25 useful as a catalyst for the production of chlorine by the

oxidation of hydrogen chloride, and it is known that the ruthenium oxide catalyst can be prepared by hydrolyzing ruthenium chloride, oxidizing the hydrolyzed product and then calcining the oxidized product. For example, US

5 Patent No. 5,871,707 describes that a ruthenium oxide catalyst supported on titanium oxide is prepared by hydrolyzing a ruthenium compound with an alkali metal hydroxide, supporting the hydrolyzed product on titanium hydroxide, and calcining the supported product under air.

10 The present inventors have found that a supported ruthenium oxide catalyst can be obtained by oxidizing a supported metal ruthenium catalyst (JP-A-10-338502). The supported metal ruthenium catalyst may be prepared by supporting ruthenium chloride on a carrier, drying the supported
15 ruthenium chloride and heating it in a hydrogen stream. However, when ruthenium chloride is reduced with hydrogen, ruthenium is sintered, and thus the supported ruthenium oxide catalyst, which is produced by oxidizing the catalyst reduced with hydrogen, has a low activity. That is a
20 problem.

Hitherto, a supported ruthenium oxide catalyst comprising titanium oxide as a carrier is known. However, from the viewpoint of a catalyst life, the development of a supported ruthenium oxide catalyst, the catalyst life of
25 which is prolonged by the improvement of the carrier, has

been sought.

Conventionally, a catalyst having a high catalytic activity can be prepared by treating a ruthenium compound, in particular, a ruthenium halide, supported on a carrier with an alkaline solution of hydrazine, but the development of a ruthenium base catalyst having a higher catalyst activity through the improvement of a preparation method has been desired. Furthermore, it is desired to develop a ruthenium oxide catalyst having a higher catalytic activity by increasing a proportion of a ruthenium oxide surface which is effective for the reaction in the ruthenium oxide particles supported on a carrier.

Next, a method for preparing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst is explained. Such a method has the same problems as those described in the above in connection with the supported ruthenium oxide catalyst. In addition to such problems, there is a problem that ruthenium oxide or a ruthenium halide supported on a carrier is sintered during a reaction and thus the catalytic activity deteriorates. Therefore, it is desired to provide a catalyst which less suffers from the sintering of ruthenium oxide or the ruthenium halide supported on the carrier during the reaction. Besides, the decrease of the steps of a process for preparing a catalyst is more preferable, and it is desired to prepare a catalyst

having a high catalytic activity by a simple process. In general, there is a problem that the activity of the catalyst decreases during the reaction. Accordingly, the development of a catalyst which less suffers from the decrease of the catalytic activity.

Now, a method for producing chlorine is explained.

It is well known that chlorine is useful as a raw material of vinyl chloride, phosgene, etc. and can be produced by oxidizing hydrogen chloride. For example, the Deacon reaction using a Cu catalyst is well known. For instance, GB Patent No. 1,046,313 discloses a process for producing chlorine comprising oxidizing hydrogen chloride in the presence of a catalyst containing a ruthenium compound, and describes that ruthenium (III) chloride is particularly effective among the ruthenium compounds. Furthermore, this GB Patent discloses the use of a ruthenium compound supported on a carrier, and exemplifies silica gel, alumina, pumice and ceramic materials as carriers. In the Examples, a ruthenium chloride catalyst supported on silica was used. However, when an experiment was carried out using a catalyst which was prepared by repeating the process for preparing (or tracing) a ruthenium (III) chloride catalyst supported on silica, which is disclosed in this GB Patent, the ruthenium compound as the catalyst component remarkably volatilized,

and therefore it was disadvantageous for industrial use.
EP 0 184 414 A2 discloses a process for producing chlorine
by oxidizing hydrogen chloride in the presence of a
chromium oxide catalyst. However, conventionally known
5 processes have a problem that the activity of the catalyst
is insufficient, and a high reaction temperature is
required.

When the activity of the catalyst is lower, a higher
reaction temperature is required. However, since the
10 reaction of oxidizing hydrogen chloride with oxygen for the
production of chlorine is an equilibrium reaction, the
higher reaction temperature is disadvantageous from the
viewpoint of equilibrium, and decreases the equilibrium
conversion of hydrogen chloride. When the catalyst has a
15 high activity, the reaction temperature can be decreased
and, therefore, the reaction becomes advantageous from the
viewpoint of the equilibrium, and the higher conversion of
hydrogen chloride can be attained. When the reaction
temperature is high, the activity of the catalyst may be
20 decreased by the volatilization of the catalyst component.
From this point of view, it has been required to develop a
catalyst which can be used at a low temperature.

For the industrial use, a catalyst is required to have
both a high activity of the catalyst and a high activity
25 per the unit mass of ruthenium contained in the catalyst.

Since the high activity per the unit mass of ruthenium contained in the catalyst can decrease the amount of ruthenium contained in the catalyst, it is advantageous from the viewpoint of a cost. It is possible to select
5 reaction conditions which are advantageous for the reaction equilibrium, when the reaction is carried out at a lower temperature using the catalyst having the higher activity. It is preferred to conduct the reaction at a lower temperature in view of the stability of the catalyst.

10 Furthermore, from the industrial point of view, a catalyst is desired, which less suffers from the decrease of the catalytic activity. It is preferred for a catalyst to have a smaller degree (or rate) of deterioration of the catalytic activity, when the change of catalytic activity
15 over time is measured. That is, a catalyst having a longer life is required.

Accordingly, the process for producing chlorine has the same problems as those described in the above in connection with the supported ruthenium oxide catalyst, and
20 also the process for preparing the supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a supported ruthenium oxide catalyst which has a high
25 catalytic activity and thus produces a desired substance in

a smaller amount at a lower temperature, and which is less sintered during the reaction, simplifies the production steps, and suffers less deactivation.

Another object of the present invention is to provide
5 a process for preparing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst which has the same characteristics as those described above.

A further object of the present invention is to provide a process for producing chlorine by oxidizing
10 hydrogen chloride with oxygen in the presence of such a supported ruthenium oxide catalyst.

According to the first aspect of the present invention, there is provided a supported ruthenium oxide catalyst selected from the group consisting of:

15 (1) a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a
20 carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50
25 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of:

5 supporting a ruthenium compound on a carrier,
calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

10 treating said calcined one with a mixed solution of hydrazine and an alkaline compound,
and

oxidizing said hydrazine-treated one.

According to the second aspect of the present
15 invention, there is provided a process for producing a supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst selected from the group consisting of the following processes (1) to (6):

(1) a process comprising the steps of:

20 supporting a ruthenium compound on a carrier consisting of titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, and

calcining said supported one in an atmosphere selected
25 from the group consisting of an oxidizing gas atmosphere,

an inert gas atmosphere and a reducing gas atmosphere;

(2) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at

5 least 200°C in an atmosphere selected from the group
consisting of an oxidizing gas atmosphere, an inert gas
atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of
hydrazine and an alkaline compound,

10 and

oxidizing said hydrazine-treated one

wherein said supported ruthenium oxide catalyst has a
carbon monoxide adsorption amount of at least 87.5 ml per
one gram of ruthenium contained in the catalyst, which is

15 measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60
minutes with flowing a hydrogen gas at a flow rate of 50
ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method

20 according to a carbon monoxide pulse;

(3) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at

least 200°C in an atmosphere selected from the group

25 consisting of an oxidizing gas atmosphere, an inert gas

atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,

and

5 oxidizing said hydrazine-treated one;

(4) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

and

10 calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein, when the peak intensity ratio of the produced catalyst and that of the catalyst after a 50 hours reaction test, which are measured by an extended X-ray absorption
15 fine structure analysis (EXAFS) method, are A(b) and B(b) respectively, the peak intensity ratios A(b) and B(b) satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that $A(b) \leq 0.8$,

20 wherein A(b) is a peak intensity ratio of as-produced Catalyst b measured by the EXAFS method, and B(b) is a peak intensity ratio of Catalyst b measured by the EXAFS method after the 50 hours reaction test;
in which

25 the 50 hours reaction test is carried out by filling

supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process, and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of

the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a process comprising the following steps but not a
5 treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide carrier containing the rutile crystal form,
and

calcining said supported one at a temperature of 200°C
10 to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere;
and

(6) a process comprising the following steps but
15 neither a calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form,
and

20 drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C.

According to the third aspect of the present invention,
25 there is provided a process for producing chlorine by

oxidizing hydrogen chloride with oxygen, which uses at least one catalyst selected from the group consisting of the following catalysts (1) to (6):

(1) a supported ruthenium oxide catalyst comprising
5 titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a
carbon monoxide adsorption amount of at least 87.5 ml per
10 one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60
minutes with flowing a hydrogen gas at a flow rate of 50
ml/min. under atmospheric pressure, and

15 conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,
20 calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of
25 hydrazine and an alkaline compound,

and

oxidizing said hydrazine-treated one;

(4) a supported ruthenium oxide catalyst produced by a process comprising the steps of:

5 supporting a ruthenium compound on a carrier,

and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein, when the peak intensity ratio of the produced catalyst and that of the catalyst after a 50 hours reaction test, which are measured by an extended X-ray absorption fine structure analysis (EXAFS) method, are A(b) and B(b) respectively, the peak intensity ratios A(b) and B(b) satisfy the following equation (1):

10

15

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that $A(b) \leq 0.8$,

wherein A(b) is a peak intensity ratio of as-produced Catalyst b measured by the EXAFS method, and B(b) is a peak intensity ratio of Catalyst b measured by the EXAFS method after the 50 hours reaction test;

20

in which

50 Hours reaction test: Supported ruthenium oxide Catalysts a and b are filled in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10

25

(Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a

particle size of at least 10 nm;

(5) a supported ruthenium oxide catalyst produced by a process comprising the following steps but not a treating step with hydrazine:

5 supporting a ruthenium compound on a titanium oxide carrier containing the rutile form,
and

calcining said supported one at a temperature of 200°C to 600°C in an atmosphere selected from the group
10 consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere;
and

(6) a supported ruthenium oxide catalyst produced by a process comprising the following steps but neither a
15 calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form,
and

drying said supported one in an atmosphere selected
20 from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C.

DETAILED DESCRIPTION OF THE INVENTION

The relationship of the catalysts described in the
25 first to third aspects of the present inventions is

explained.

As a typical example, the relationship of the catalysts (1) through (6) in the third aspect of the present invention is explained.

5 For example, the catalyst (1) of the third aspect of the present invention, that is, a supported ruthenium oxide catalyst comprising titanium oxide which contains the
10 rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier, is a preferred example of the catalysts (2) and (6) of the third aspect of the present invention.

15 The catalyst (3) of the third aspect of the present invention is prepared by the process comprising four steps, that is, the steps of supporting a ruthenium compound on a carrier, calcining said supported one at a temperature of
20 at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, treating said calcined one with a mixed solution of hydrazine and an alkaline compound, and oxidizing said hydrazine-treated one.
25 However, a catalyst, which is prepared by a process comprising one or two steps of the above four steps, has also its own characteristics, as it is presented as the catalyst from (4) to (6) of the third aspect of the present invention.

As shown in the catalyst which is prepared by the process comprising two steps, that is, the steps of supporting a ruthenium compound on a carrier, calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, has its own characteristics, as it is presented as the catalyst (4), (5) of the third aspect of the present invention.

Furthermore, a catalyst, which is prepared by a process comprising the one step, has its own characteristics, as it is presented as the catalyst (6) of the third aspect of the present invention.

Hereinafter, the inventions of the first to third aspects will be explained.

The catalyst (1) of the first aspect of the present invention is a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier.

The calcination temperature is preferably from 550 to 1,000°C, more preferably from 600 to 1,000°C, particularly preferably from 700 to 1,000°C, most preferably from 800 to 1,000°C.

When such a carrier is used, a catalyst which suffers

from less deactivation in comparison with the conventional ones can be obtained.

Here, a test method for a reaction to obtain chlorine by oxidizing hydrogen chloride is explained.

5 As a material of a test reaction tube, nickel, glass, quartz glass, and the like can be used. Since reaction gasses and formed gasses are corrosive, some special cares should be taken when other material is used. When the catalyst has a high activity, the heat of reaction cannot
10 be removed from the reaction tube. In such a case, the catalyst is diluted with a carrier such as α -alumina balls and then filled in the reaction tube to increase the heat-removing efficiency. When the heat conductivity of the catalyst layer in the reactor tube is insufficient, the
15 heat of reaction is not removed and thus the temperature locally rises and the reaction temperature may not be suitably controlled so that the correct test may not be performed. When a plurality of layers of the catalysts are filled in the reactor tube, a respective temperature can be
20 set with each catalyst layer. In general, the catalyst temperature is in the range between 250 and 450°C.

Now, the preparation example of the catalyst according to the present invention is explained.

25 The supported ruthenium oxide catalyst may be prepared by treating a ruthenium compound supported on a carrier

with a reducing compound or a mixture of a reducing compound and a base compound, and oxidizing the treated ruthenium compound supported on the carrier.

Typically, titanium oxide containing rutile
5 crystalline titanium oxide is used as a carrier.

In general, titanium oxide includes rutile crystalline titanium oxide, anatase crystalline titanium oxide, non-crystalline titanium oxide, etc.

Titanium oxide containing rutile crystal form used in
10 the present invention means titanium oxide containing the rutile crystal, when the ratio of the rutile crystal to the anatase crystal in titanium oxide is measured by the X-ray diffraction analysis. This analysis will be explained in detail below.

15 When the chemical composition of the carrier used in the present invention consists of titanium oxide, the proportion of the rutile crystal can be determined from the ratio of the rutile crystal and the anatase crystal in titanium oxide measured by the X-ray diffraction analysis.
20 However, since the carrier may contain a mixed oxide of titanium oxide and other metal oxide, in such a case, the content of the rutile crystal can be determined as described below.

The oxide to be mixed with the titanium oxide include
25 oxide of elements, and preferred examples of oxides include

alumina, zirconium oxide, silica, etc. The proportion of the rutile crystal in the mixed oxide is also determined from the ratio of the rutile crystal to the anatase crystal in titanium oxide measured by the X-ray diffraction analysis. In the present invention, titanium oxide should contain the rutile crystal. In this case, the content of the metal oxide other than titanium oxide is from 0 to 60 mass %. Preferably, the carrier does not contain any metal oxide other than titanium oxide.

10 Titanium oxide should contain the rutile crystal. The proportion of the rutile crystal is preferably at least 10 %, more preferably at least 30 %, in particular at least 80 %.

Various methods are known to prepare titanium oxide containing the rutile crystal. In general, the following preparation method is used.

When titanium tetrachloride is used as a raw material, titanium tetrachloride is dropwise added to ice-cooled water and neutralized with aqueous ammonia to form titanium hydroxide (orthotitanic acid). Then, the formed precipitate is washed with water to remove chloride ions. In such a process, when the temperature in the course of the neutralization rises to a high temperature of 20°C or higher, or the chloride ions remain in titanium oxide after washing, titanium hydroxide can be easily converted to

rutile crystalline titanium oxide by calcination. When the calcination temperature is 600°C or higher, titanium oxide easily becomes the rutile crystal type ("SHOKUBAI CHOUSEI KAGAKU" (Catalyst Preparation Chemistry), 1989, page 211 published by KODANSHA).

Alternatively, a mixed gas of oxygen and nitrogen is introduced in an evaporator for titanium tetrachloride to prepare a reaction gas, which is introduced in a reactor. The reaction between titanium tetrachloride and oxygen starts at a temperature around 400°C, and titanium dioxide synthesized by the reaction of TiCl_4 and O_2 at such a temperature is mainly the anatase type. When the reaction temperature rises to 900°C or higher, the rutile type titanium oxide forms ("SHOKUBAI CHOUSEI KAGAKU" (Catalyst Preparation Chemistry), 1989, page 89 published by KODANSHA).

Furthermore, the following methods may be used:

a method comprising hydrolyzing titanium tetrachloride in the presence of ammonium sulfate and calcining the hydrolyzed product (for example, "SHOKUBAI KOGAKU KOZA" (Catalyst Engineering Lectures) 10, "GENSOBETSU SHOKUBAI BINRAN" (ELEMENT-BY-ELEMENT CATALYST HANDBOOK), 1978, page 254 published by CHIJIN SHOKAN); a method comprising calcining anatase crystalline titanium oxide (for example, "KINZOKU SANKABUTU TO FUKUGO SANKABUTU" (Metal Oxides and

Mixed oxides), 1980, page 107 published by KODANSHA); etc.

Rutile crystalline titanium oxide may be prepared by thermally hydrolyzing an aqueous solution of titanium tetrachloride.

5 In addition, rutile crystalline titanium oxide may be prepared by firstly mixing an aqueous solution of a titanium compound (e.g. titanium sulfate, titanium chloride, etc.) and rutile crystalline titanium oxide powder, thermally hydrolyzing or alkali hydrolyzing the mixture,
10 and then calcining the hydrolyzed product at a relatively low temperature of around 500°C.

As described above, the ratio of the rutile crystal in titanium oxide can be determined by the X-ray diffraction analysis. As an X-ray source, various types of the source
15 such as the $K\alpha$ ray of copper may be used. When the $K\alpha$ ray of copper is used, the proportions of the rutile crystal and the anatase crystal can be determined from the intensity of the diffraction peak of the (110) plane at 2θ
= 27.5 degrees, and that of the diffraction peak of the
20 (101) plane at 2θ = 25.3 degrees in the X-ray diffraction pattern.

The titanium oxide carrier to be used in the present invention includes one having the peak intensity of the rutile crystal and that of the anatase crystal, or one
25 having the peak intensity of the rutile crystal only. That

is, titanium oxide may be one having the diffraction peak assigned to the rutile crystal and that assigned to the anatase crystal, or one having only the diffraction peak assigned to the rutile crystal. In preferred titanium
5 oxide, a ratio of the peak intensity of the rutile crystal to the sum of the peak intensity of the rutile crystal and that of the anatase crystal is at least 10 %.

Specific methods for the preparation of the catalyst will be explained later in connection with the catalyst (3)
10 according to the first aspect of the present invention.

The supported ruthenium oxide catalyst (2) according to the first aspect of the present invention is a supported ruthenium oxide catalyst having a carbon monoxide adsorption amount of at least 87.5 ml per one gram of
15 ruthenium contained in the catalyst, which is measured by the steps of reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and conducting a metal surface area measuring method according to a carbon
20 monoxide pulse.

The details of the MSA measuring method will be explained in the Examples.

The adsorbed amount of carbon monoxide per the unit mass of ruthenium correlates with the metal surface area
25 (MSA) of ruthenium, which, in turn, correlates with the

surface area of ruthenium oxide prior to the reduction. Furthermore, the surface area of ruthenium oxide correlates with the number of active sites of catalytically active ruthenium oxide.

5 The activity of the supported ruthenium oxide catalyst corresponds to the number of active sites of ruthenium oxide, but it is difficult to directly measure the surface area of ruthenium oxide corresponding to the number of the active sites. However, it is possible to measure the metal
10 surface area by reducing the catalyst to form metal ruthenium and then adsorbing carbon monoxide on the metal ruthenium. In this case, to maintain the correlation between the surface area of ruthenium oxide on the carrier and the surface area of metal ruthenium after the reduction,
15 it is a prerequisite that ruthenium is not sintered by the reduction with hydrogen.

 Thus, the present inventors investigated the reducing conditions of the supported ruthenium oxide catalyst. As a result, it has been found that ruthenium oxide can be
20 reduced without being sintered, when 220°C is selected as a reducing temperature from the range between 150°C and 250°C, one hour is selected as a reducing time, and a heating rate of 20°C/min. and a hydrogen flow rate of 50 ml/min. are determined.

25 The amount of carbon monoxide adsorbed on reduced

ruthenium has a specific relationship with the surface area of metal ruthenium.

Accordingly, as an index of the activity of the supported ruthenium oxide catalyst, a method for measuring the amount of adsorbed carbon monoxide has been established, which method comprises the steps of:

reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse.

In general, the supported ruthenium oxide catalyst (2) has a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst (ml/g-Ru). Preferably, the carbon monoxide adsorption amount is from 90 to 200 ml/g-Ru, more preferably from 92.5 to 150 ml/g-Ru.

Various methods may be used to prepare the supported ruthenium oxide catalyst having the larger number of active sites of ruthenium oxide. Some specific methods will be explained, but the catalyst (2) of the first aspect of the present invention can be produced by the process employed to prepare the catalyst (3) of the first aspect of the present invention.

Hereinafter, the catalyst (3) of the first aspect of

the present invention will be explained. The catalyst (3) of the first aspect of the present invention is one example of the catalyst (2) of the first aspect of the present invention.

5 The supported ruthenium oxide catalyst (3) of the first aspect of the present invention is one prepared by the process comprising the steps of:

supporting a ruthenium compound on a carrier,

10 calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,

15 and

oxidizing said hydrazine-treated one.

Firstly, the step to support a ruthenium compound on a carrier is explained.

20 Examples of the carrier include oxides and mixed oxides of elements such as titanium oxide, alumina, zirconium oxide, silica, titanium mixed oxide, zirconium mixed oxide, aluminum mixed oxide, silicon mixed oxide, etc. Preferred carrier are titanium oxide, alumina, zirconium oxide and silica. Among them, titanium oxide is more
25 preferred.

A particularly preferred carrier is titanium oxide containing rutile crystalline titanium oxide.

Such titanium oxide containing rutile crystalline titanium oxide has been explained in the above in
5 connection with the catalyst (1) of the first aspect of the present invention.

In the case of the supported ruthenium oxide catalyst comprising titanium oxide containing rutile crystalline titanium oxide as a carrier, its catalytic activity can be
10 increased by the optimization of the amount of OH groups contained in the carrier. In general, it is known that hydroxyl (OH) groups bonded to titanium atoms are present on the surface of titanium oxide. In the present invention, used titanium oxide contains the OH groups. A method for
15 measuring the amount of the OH groups will be explained in detail below.

The amount of the OH groups contained in the carrier can be determined from the amount of the OH groups in titanium oxide, when the chemical composition of the
20 carrier used in the present invention consists of titanium oxide only. However, the carrier may be a mixed oxide of titanium oxide and other metal oxide. Preferred examples of the other metal oxide include alumina, zirconium oxide, silica, etc. In such a case, the content of the metal
25 oxide other than titanium oxide is from 0 to 60 mass %. In

this case, the amount of the OH group contained in the unit mass of the carrier can be measured by the method, which will be explained in detail below. Preferably, the carrier does not contain any metal oxide other than titanium oxide.

5 When the amount of the OH groups is too large, the carrier and supported ruthenium oxide react each other, and thus the catalyst may be deactivated. When the amount of the OH group is too small, the activity of the catalyst may be decreased by the sintering of supported ruthenium oxide
10 or other phenomena. That is, the OH groups are contained in an amount in a suitable range depending the amount of the ruthenium compound to be supported on the carrier, and the catalytic activity gradually increases as the amount of the OH group increases in such a range, and tends to
15 decrease after it reaches the peak activity. Therefore, the catalyst exhibits a high activity in the suitable range of the amount of the OH groups.

20 The amount of the OH groups contained in the titanium oxide carrier used in the catalyst of the present invention is generally from 0.1×10^{-4} to 30×10^{-4} mol/g-carrier, preferably from 0.2×10^{-4} to 20×10^{-4} mol/g-carrier, more preferably from 3.0×10^{-4} to 10×10^{-4} mol/g-carrier.

25 There are various methods for determining the amount of the OH groups contained in titanium oxide. A preferred method is a titration method using an alkyl alkali metal.

Preferably, the titration method using the alkyl alkali metal comprises suspending the titanium oxide carrier or the titanium oxide carrier powder in a dehydrated solvent, dropwise adding the alkyl alkali metal in a nitrogen atmosphere, and calculating the amount of the OH group contained in titanium oxide from the amount of a generated hydrocarbon. In this method, water remained in the dehydrated solvent reacts with the alkyl alkali metal to generate the hydrocarbon. Therefore, the amount of the hydrocarbon generated by the reaction of residual water and the alkyl alkali metal should be deducted from the total amount of the hydrocarbon to obtain the correct amount of the OH groups contained in titanium oxide.

In the most preferred embodiment of the above titration method, the titanium oxide carrier or the titanium oxide carrier powder is suspended in dehydrated toluene, methyl lithium is dropwise added to the suspension in the nitrogen atmosphere, and then the amount of the OH group contained in titanium oxide is calculated from the amount of generated methane. The amount of the OH groups contained in titanium oxide, which is defined in this specification, is measured by this most preferred method.

For example, the measuring steps are as follows:

Firstly, a sample is dried under air at 150°C for 2 hours, and cooled in a desiccater. Then, a specific amount

of the sample is transferred to a flask which has been replaced with nitrogen, and suspended in an organic solvent such as dehydrated toluene. Into the suspension, methyl lithium is dropwise added while cooling the flask with ice
5 to suppress the heat generation, and the generated gas is trapped and its volume is measured at a measuring room temperature.

The process of adjusting the amount of the OH groups contained in the titanium oxide carrier to a predetermined
10 amount includes various process. For example, a temperature and/or time to calcine the carrier can be controlled for this purpose. The OH groups can be eliminated from the titanium oxide carrier by heating, and the calcination temperature or time can be changed to
15 control the amount of the OH groups in the titanium oxide carrier.

The calcination temperature of the carrier is usually from 100 to 1,000°C, preferably from 150 to 800°C, and the calcination time of the carrier is usually from 30 minutes
20 to 12 hours. In the calcination step, it should be noted that the surface area of the carrier decreases as the calcination temperature rises, or the calcination time is prolonged.

Furthermore, when titanium oxide is produced in a gas
25 phase, one containing the small amount of the OH group can

be produced, while when titanium oxide is produced in an aqueous phase such as an aqueous solution, one containing the large amount of the OH group can be produced.

Examples of the ruthenium compound to be supported on the carrier include ruthenium chlorides such as RuCl_3 , RuCl_3 hydrate, etc.; chlororuthenate salts such as K_3RuCl_6 , $(\text{RuCl}_6)^{3-}$, K_2RuCl_6 , etc.; chlororuthenate salt hydrates such as $[\text{RuCl}_5(\text{H}_2\text{O})_4]^{2-}$, $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$, etc.; ruthenate salts such as K_2RuO_4 , etc.; ruthenium oxychlorides such as Ru_2OCl_4 , Ru_2OCl_5 , Ru_2OCl_6 , etc.; salts of ruthenium oxychlorides such as $\text{K}_2\text{Ru}_2\text{OCl}_{10}$, $\text{Cs}_2\text{Ru}_2\text{OCl}_4$, etc.; ruthenium-ammine complexes such as $[\text{Ru}(\text{NH}_3)_6]^{2+}$, $[\text{Ru}(\text{NH}_3)_6]^{3+}$, $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$, etc.; chlorides and bromides of ruthenium-ammine complexes such as $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Ru}(\text{NH}_3)_6]\text{Br}_3$, etc.; ruthenium bromides such as RuBr_3 , RuBr_3 hydrate, etc.; other ruthenium-organoamine complexes; ruthenium-acetylacetonato complexes; ruthenium-carbonyl complexes such as $\text{Ru}(\text{CO})_5$, $\text{Ru}_3(\text{CO})_{12}$, etc.; organic acid salts of ruthenium such as $[\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{H}_2\text{O})_3]\text{OCOCH}_3$ hydrate, $\text{Ru}_2(\text{RCOO})_4\text{Cl}$ in which R is an alkyl group having 1 to 3 carbon atoms, etc.; ruthenium-nitrosyl complexes such as $\text{K}_2[\text{RuCl}_5(\text{NO})]$, $\text{Ru}[(\text{NH}_3)_5(\text{NO})]\text{Cl}_3$, $[\text{Ru}(\text{OH})(\text{NH}_3)_4(\text{NO})](\text{NO}_3)_2$, $\text{Ru}(\text{NO})(\text{NO}_3)_3$, etc.; ruthenium-phosphine complexes; and the like. Preferred examples of the ruthenium compound include ruthenium halides, for example, ruthenium chlorides such as

RuCl_3 , RuCl_3 hydrate, etc., and ruthenium bromides such as RuBr_3 , RuBr_3 hydrate, etc. More preferably, ruthenium chloride hydrate is used.

5 The process for supporting the ruthenium compound on the carrier includes an impregnation process, an equilibrium adsorption process, etc.

Next, the calcining step is explained.

10 In the calcining step, the ruthenium compound-supported one, which is obtained in the previous ruthenium compound-supporting step, is calcined at a temperature of at least 200°C in an atmosphere selected from the group consisting an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

15 Examples of the inert gas include nitrogen, helium, etc. Examples of the oxidizing gas include air, oxygen, a mixture of nitrogen and oxygen, etc. Examples of the reducing gas include hydrogen, a mixture of hydrogen and nitrogen, etc.

20 In this step, the ruthenium compound-supported one is dried, and then the ruthenium compound is fixed on the carrier, so that the ruthenium compound can be stably treated in the subsequent hydrazine-treating step.

25 When the catalyst produced by the process including this calcination step is compared with a catalyst produced by the same process but including no calcination step, the

treatment with hydrazine is considerably stably conducted, so that the catalytic activity increases. Preferably, the ruthenium compound-supported one is calcined in the oxidizing gas atmosphere, more preferably, under air.

5 Hereinafter, the hydrazine-treating step is explained.

The hydrazine-treating step includes that the calcined one from the previous calcination step is treated with hydrazine by dipping the calcined one in a mixed solution of hydrazine and an alkali, or impregnating the calcined one with such a mixed solution.

10

Examples of the alkali to be used include aqueous solutions of hydroxides, carbonates or hydrogen carbonates of alkali metals, ammonia, ammonium carbonate, ammonium hydrogen carbonate, etc.; solutions of these alkali compounds in organic solvents such as alcohol; and the like.

15

Preferred examples of the alkali include hydroxides, carbonates and hydrogen carbonates of alkali metals.

Preferred examples of the solvent include water.

In addition, except treating with hydrazine, another preferred method is exemplified. Another preferred method comprises reducing the calcined one from the calcination step, in a liquid phase.

20

Examples of reducing agents include methanol or formaldehyde; aqueous solutions and organic solvent solutions of methanol or formaldehyde; hydrogen; boron

25

hydride compounds such as NaBH_4 , $\text{Na}_2\text{B}_2\text{H}_6$, $\text{Na}_2\text{B}_4\text{H}_{10}$, $\text{Na}_2\text{B}_5\text{H}_9$, LiBH_4 , $\text{K}_2\text{B}_2\text{H}_6$, $\text{K}_2\text{B}_4\text{H}_{10}$, $\text{K}_2\text{B}_5\text{H}_9$, $\text{Al}(\text{BH}_4)_3$, etc.; organometallic boron hydride compounds such as $\text{LiB}[\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5]_3\text{H}$, $\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$, $\text{KB}[\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5]_3\text{H}$, $\text{KB}[\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2]_3\text{H}$, etc.;
 5 metal hydrides such as LiAlH_4 , NaH , LiH , KH , etc.; organoaluminum compounds such as $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{Al}$, etc.; organolithium compounds; organosodium compounds; organopotassium compounds; organomagnesium compounds; and the like.

10 It is also preferable to add an alkali metal chloride after the treatment with hydrazine or the reducing agent.

The oxidizing process includes a process comprising calcining the treated one under air.

A weight ratio of ruthenium oxide to the carrier is
 15 preferably from 0.1:99.9 to 20.0:80.0, more preferably from 0.5:99.5 to 15.0:85.0, in particular from 1.0:99.0 to 15.0:85.0.

When the ratio of ruthenium oxide is too low, the activity of the produced catalyst may decrease. When the
 20 ratio of ruthenium oxide is too high, the cost of the catalyst may increase.

Ruthenium oxide is preferably ruthenium dioxide or ruthenium oxide hydrates. Alternatively, ruthenium hydroxide may be used as a precursor of ruthenium oxide.

25 A preferable example of the process for preparing the

supported ruthenium oxide catalyst (3) of the first aspect of the present invention is a process comprising the steps of:

supporting a ruthenium halide on a carrier,
5 calcining the supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

10 treating the calcined one with a mixed solution of hydrazine and an alkaline compound,
and

oxidizing the hydrazine-treated one.

A more preferable example of the process for preparing the supported ruthenium oxide catalyst (3) of the first
15 aspect of the present invention is a process comprising the steps of:

supporting a ruthenium halide on a carrier,
calcining the supported one at a temperature of at
least 200°C in an atmosphere selected from the group
20 consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating the calcined one with a mixed solution of hydrazine and an alkaline compound,

25 adding an alkali metal halide to the hydrazine-treated one,

and

oxidizing the alkali metal halide-added one.

In the first step of the above preferred embodiment, a ruthenium halide is supported on a carrier.

5 As the ruthenium halides, those exemplified in the above may be used. Among them, ruthenium chlorides such as RuCl_3 , RuCl_3 hydrate and ruthenium bromide such as RuBr_3 , RuBr_3 hydrate are preferred. In particular, ruthenium chloride hydrate is preferred.

10 The amount of the ruthenium halide to be used in the step for supporting the ruthenium halide on the carrier is an amount satisfying a preferred weight ratio of ruthenium oxide to the carrier.

15 The ruthenium halide may be supported on the carrier by impregnating the catalyst carrier, which is explained in the above, with the solution of the ruthenium halide, or supporting the ruthenium halide on the carrier by the equilibrium absorption.

20 As a solvent, water or an organic solvent such as an alcohol is used. Preferably, water is used.

25 Next, the impregnated carrier may be dried or may not be dried. Preferably, it is dried. This drying is carried out to remove the solvent from the impregnated solution of the ruthenium halide, and it has the different purpose from the subsequent calcination and should be distinguished from

the calcination which is done in the subsequent step.

In the calcination step, the carrier supporting the ruthenium halide is calcined at a temperature of at least 200°C in an atmosphere selected from the group consisting
5 an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

Examples of the inert gas include nitrogen, helium, etc. Examples of the oxidizing gas include air, oxygen, a mixture of nitrogen and oxygen, etc. Examples of the
10 reducing gas include hydrogen, a mixture of hydrogen and nitrogen, etc.

Preferably, the calcination is carried out in the oxidizing gas atmosphere. More preferably, the calcination is carried out under air.

15 The calcination temperature is at least 200°C. However, when the calcination temperature is too high, the supported ruthenium halide is sintered, so that the activity of the resulting catalyst tends to decrease. Thus, the calcination temperature is preferably from 200 to 350°C,
20 more preferably from 200 to 300°C.

In the hydrazine-treating step, the product from the calcination step is treated with the mixed solution of hydrazine and an alkali. The treatment with the mixed solution of hydrazine and the alkali can be carried out by
25 dipping the calcined one in such a mixed solution, or

impregnating the carrier with such a mixed solution.

The concentration of hydrazine used in the hydrazine-treating step is preferably at least 0.1 mol/l. Hydrazine is used in the form of a solution in water or an organic solvent such as an alcohol, while hydrazine hydrate such as hydrazine monohydrate may be used as such. Preferably, the aqueous solution of hydrazine, or hydrazine hydrate is used. Hydrazine may be anhydrous hydrazine or hydrazine hydrate.

A molar ratio of the ruthenium halide to hydrazine is preferably from 1:0.1 to 1:20. In the case of sodium hydroxide, 3 moles of sodium hydroxide per one mole of the ruthenium halide is an equimolar amount. Preferably, the alkali is used in the amount of 0.1 to 20 equivalent per equivalent of ruthenium halide.

The concentration of the alkali varies with the kind of the alkali, and is preferably from 0.1 to 10 mol/l.

The time to dip the calcined product in the mixed solution of hydrazine and the alkali is preferably from 5 minutes to 5 hours. The dipping temperature is preferably from 0 to 100°C, more preferably from 10 to 60°C. After dipping, the treated product is filtrated to separate the solution.

In a preferred embodiment of the above process, the product from the hydrazine-treating step is washed with water to remove the alkali and hydrazine, dried, and then

added with an alkali metal chloride in the subsequent step to add the alkali metal chloride, followed by drying and oxidizing.

5 In a more preferred embodiment, the product from the hydrazine-treating step is washed with an aqueous solution of an alkali metal chloride, dried and then oxidized. In this embodiment, the removal of the alkali and hydrazine and the addition of the alkali metal chloride can preferably be carried out in the same step.

10 In the alkali metal chloride-adding step, the alkali metal chloride is added to the product from the hydrazine-treating step. This step may not be essential to the preparation of the supported ruthenium oxide catalyst, but this step can further increase the activity of the catalyst.
15 That is, in the subsequent oxidizing step, the hydrazine-treated catalyst is oxidized in the presence of the alkali metal chloride to obtain the supported ruthenium oxide catalyst having the higher activity.

Examples of the alkali metal chloride include
20 potassium chloride, sodium chloride, etc. Preferably, potassium chloride or sodium chloride is used, and more preferably potassium chloride is used.

A molar ratio of the alkali metal chloride to ruthenium is preferably from 0.01:1 to 10:1, more
25 preferably from 0.1:1 to 5.0:1. When the amount of the

alkali metal chloride is too small, the catalyst having the sufficiently high activity may not be obtained. When the amount of the alkali metal chloride is too large, the production cost of the catalyst increases in the industrial
5 production.

To add the alkali metal chloride, the hydrazine-treated ruthenium catalyst, which has been washed and dried, is impregnated with the aqueous solution of the alkali metal chloride. More preferably, the hydrazine-treated
10 ruthenium catalyst is washed with the aqueous solution of the alkali metal chloride instead of water and impregnated with the same aqueous solution.

It may be possible to add hydrochloric acid to the aqueous solution of the alkali metal chloride to adjust pH
15 in the course of washing of the catalyst.

The concentration of the aqueous solution of the alkali metal chloride is preferably from 0.01 to 10 mol/l, more preferably from 0.1 to 5 mol/l.

The purpose of the washing is to remove the alkali and
20 hydrazine, although the alkali and hydrazine may remain on the catalyst to the extent that the effects of the present invention are not impaired.

After the impregnation of the alkali metal chloride, the catalyst is usually dried. Preferably, the drying
25 conditions include a temperature of 50 to 200°C, and a time

of 1 to 10 hours.

The oxidation step is a step for oxidizing the product from the hydrazine-treating step (when the step to add the alkali metal chloride is not used), or a step for oxidizing the product from the alkali metal chloride-adding step (when the step to add the alkali metal chloride is used).

It is a preferable preparation example to convert it into highly active supported ruthenium oxide by calcining one treated with the alkali and hydrazine in the presence of an alkali metal salt, in a gas containing oxygen. An example of the oxygen-containing gas is usually an air.

The calcination temperature is preferably from 100 to 600°C, more preferably from 280 to 450°C. When the calcination temperature is too low, many particles generated by the treatment with hydrazine may remain in the form of a ruthenium oxide precursor and thus the obtained catalyst may have an insufficient activity. When the calcination temperature is too high, the ruthenium oxide particles tend to agglomerate, so that the catalytic activity deteriorates.

The calcination time is preferably from 30 minutes to 10 hours.

In this step, it is preferable and important to carry out the calcination in the presence of the alkali metal chloride. By this method, ruthenium oxide having a smaller

particle size is obtained, so that the higher catalytic activity is achieved than a catalyst prepared by the calcination substantially in the absence of the alkali metal chloride.

5 By the calcination, the particles supported on the carrier, which have been generated by the treatment with hydrazine, are converted to the supported ruthenium oxide catalyst.

10 The conversion of the particles generated by the treatment with hydrazine to ruthenium oxide can be confirmed by an analysis such as X-ray diffraction, XPS (X-ray photoelectron spectroscopy), etc.

15 In the particles generated by the treatment with hydrazine, preferably, substantially all the particles are converted to ruthenium oxide, although some particles may remain unconverted insofar as the effects of the present invention are not impaired.

20 In addition, in a preferred embodiment, after the oxidation step, the catalyst is washed with water to remove the residual alkali metal chloride, and dried. It is preferable to thoroughly wash off the alkali metal chloride which is present in the oxidation step.

25 The residual amount of the alkali metal chloride after washing can be measured by adding an aqueous solution of silver nitrate and checking the formation of white

turbidity. The alkali metal chloride may remain in the catalyst to an extent such that the activity of the catalyst of the present invention may not be deteriorated.

Preferably, the washed catalyst is dried. Preferably,
5 the drying conditions include a temperature of 50 to 200°C, and a time of 1 to 10 hours.

The supported ruthenium oxide catalyst, which is prepared by the above-described process has a high activity and is more active than a catalyst prepared by reducing
10 ruthenium chloride with hydrogen and oxidizing it. Furthermore, the catalyst, which is obtained by pretreating the ruthenium compound with the alkali, treating the product with hydrazine, and then oxidizing the hydrazine-treated product, has a higher activity than a catalyst
15 prepared by treating ruthenium chloride with hydrazine and oxidizing the hydrazine-treated product.

Hereinafter, the process for producing the supported ruthenium oxide catalyst or a supported ruthenium chloride catalyst of the second aspect of the present invention is
20 explained.

The process (1) of the second aspect of the present invention comprises the steps of:

supporting a ruthenium compound on a carrier consisting of titanium oxide which contains the rutile
25 crystal form, and which is obtained by calcination at a

temperature of at least 550°C, and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

5 The detailed explanation of this process is already made in connection with the catalyst (1) of the first aspect of the present invention.

Next, the process (2) of the second aspect of the present invention comprises the steps of:

10 supporting a ruthenium compound on a carrier,
calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

15 treating said calcined one with a mixed solution of hydrazine and an alkaline compound,
and

oxidizing said hydrazine-treated one wherein said supported ruthenium oxide catalyst has a
20 carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50
25 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse.

The detailed explanation of this process is already made in connection with the catalysts (2) and (3) of the first aspect of the present invention.

The process (3) of the second aspect of the present invention comprises the steps of:

supporting a ruthenium compound on a carrier,
calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,
and

oxidizing said hydrazine-treated one.

The detailed explanation of this process is already made in connection with the catalyst (3) of the first aspect of the present invention.

The process (4) of the second aspect of the present invention comprises the steps of:

supporting a ruthenium compound on a carrier,
and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere,

an inert gas atmosphere and a reducing gas atmosphere, wherein, when the peak intensity ratio of the produced catalyst and that of the catalyst after a 50 hours reaction test, which are measured by an extended X-ray absorption fine structure analysis (EXAFS) method, are A(b) and B(b) respectively, the peak intensity ratios A(b) and B(b) satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that $A(b) \leq 0.8$,

wherein A(b) is a peak intensity ratio of as-produced Catalyst b measured by the EXAFS method, and B(b) is a peak intensity ratio of Catalyst b measured by the EXAFS method after the 50 hours reaction test; in which

the 50 hours reaction test is carried out by filling supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat.,

which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced
5 by the above process,
and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst
10 is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium
15 atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm.

The reaction test for forming chlorine, which is
20 carried out by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, may be conducted as follows:

The supported ruthenium oxide catalyst (2.5 g) is well mixed with a commercially sold spherical α -alumina carrier
25 having a diameter of 2 mm (SSA 995 manufactured by NIKKATO

Co., Ltd.) (10 g) to dilute the catalyst, and then charged in a quartz reactor tube having an inner diameter of 12 mm. In the reactor tube, hydrogen chloride gas and oxygen gas are supplied at flow rates of 192 ml/min. and 192 ml/min., respectively (each converted to a volume at 0°C under 1 atm.)

The quartz reactor tube is heated with an electric furnace to adjust the internal temperature (hot spot) to 300°C.

When 2 hours lapses from the start of the reaction, the gas from the outlet of the reactor tube is sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride are determined by iodometric titration and neutralization titration, respectively.

Then, a chlorine formation activity per unit mass of the catalyst is calculated according to the following equation:

$$\text{Chlorine formation activity (mol/min.g-cat.)} = \frac{\text{Amount of outlet chlorine formed per unit time (mol/min.)}}{\text{weight of catalyst (g)}}$$

Furthermore, it has been found that the peak intensity ratio of the supported ruthenium oxide catalyst, which is explained below, corresponds to the structure of ruthenium oxide supported on the carrier and correlates with the

catalyst activity. The peak intensity ratio is obtained by dividing the peak intensity corresponding to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide carried on the support which is measured by the EXAFS method (a
5 numerator) by the peak intensity of ruthenium oxide having a particle size of at least 10 nm (a denominator).

That is, when the peak intensity ratio of the spectrum corresponding to the number of the second nearest neighbor
10 ruthenium atoms of ruthenium atoms in ruthenium dioxide, which is obtained from the peak intensity around 0.32 nm in a radial distribution function, is used and the form of ruthenium dioxide is assumed, the size of the ruthenium dioxide block can be obtained. In this case, the
15 preferable size of the ruthenium dioxide block depends on the assumed form of ruthenium dioxide. When the peak intensity ratio is calculated with the peak intensity of the spectrum corresponding to the number of the second nearest neighbor ruthenium atoms of ruthenium atoms in
20 ruthenium dioxide being a numerator, and the peak intensity of ruthenium oxide having the particle size of 10 nm or more being a denominator, the peak intensity ratio of 0.8 or less correspond to the size of the ruthenium dioxide block desirable for the supported ruthenium oxide catalyst
25 of the present invention.

Furthermore, when the peak intensity ratio of the catalyst prior to the reaction is compared with that of the catalyst after the reaction, the change of the size of the ruthenium dioxide block can be monitored, and thus the progress of the sintering of ruthenium oxide on the carrier can be measured.

That is, in one preferred embodiment, the present invention provides a process for producing a catalyst in which the ratio of the above defined peak intensity ratio before the reaction to that after the reaction is 1.45 or less. The specific procedures of such a process will be explained below.

One of the characteristics of the catalyst according to the present invention is that ruthenium oxide is less sintered when the above-defined specific ruthenium oxide catalyst is used in the production process of the desired product, that is, chlorine using a supported ruthenium oxide catalyst.

In the present invention, the above-defined ratio $B(b)/A(b)$ is preferably 1.40 or less, more preferably 1.25 or less. $A(b)$ is preferably 0.7 or less.

Here, a general procedure of the X-ray absorption fine structure analysis (XAFS) method is explained. The principle and analysis method of XAFS are described in detail in, for example, X-Ray Absorption. Principles,

Applications, Techniques of EXAFS, SEXAFS and XANES" edited by D.C. Koningsberger and R. Prins (1988).

When a material is placed on a beam line of X-ray, an X-ray absorbanace of the material is calculated from the intensity of the irradiated X-ray (incident X-ray: I_0) and the intensity of X-ray which passes through the material (transmitted X-ray: I_t). When an X-ray absorption spectrum is recorded while the energy of X-ray is changed with monitoring the increase or decrease of the X-ray absorbance, an abrupt standing of the X-ray absorbance (absorption edge) is observed at a certain X-ray energy level. Fine oscillatory structures, which appear in the range on the high energy side that is about 30 to 1,000 eV higher than the energy of the absorption edge, are extended X-ray absorption fine structures. The fluctuation of the X-ray absorption probability is caused by the interference between photoelectron waves emitted from the absorbing atom by the absorption of X-ray and photoelectron waves which are scattered by and returning from atoms surrounding the absorbing atom. Thus, the information on the local structure near the absorbing atom can be obtained when the fluctuation of the X-ray absorption probability is extensively analyzed.

A radial distribution function around the X-ray absorbing atom is obtained, when the EXAFS spectrum, which

is extracted from the X-ray absorption spectrum is subjected to the Fourier transformation in a suitable range. When this radial distribution function is examined in detail, the position of the maximum of this function provides the information on the distance between the absorbing atom and the scattering atom, and the intensity of the maximum provides the information on the number of the scattering atoms. Thus, the structural information near the noted absorbing atom can be gathered.

Hereinafter, the concrete procedures of the process (4) of the second aspect of the present invention will be explained. The process (4) comprises the steps of supporting a ruthenium compound on a carrier, and calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

Firstly, the step to support a ruthenium compound on a carrier is explained.

As a carrier, the same carrier as that used in the process (3) of the second aspect of the present invention can be used.

Titanium oxide containing rutile crystalline titanium oxide, which is preferably used in the present invention, means titanium oxide containing the rutile crystal, when the ratio of the rutile crystal to the anatase crystal in

titanium oxide is measured by the X-ray diffraction analysis. This analysis is explained in connection with the catalyst (1) of the first aspect of the present invention.

5 Titanium oxide should contain the rutile crystal. The proportion of the rutile crystal is preferably at least 10 %, more preferably at least 30 %, in particular at least 80 %.

10 In one preferred embodiment, titanium oxide contains OH groups in an amount which is explained in connection with the catalyst (3) of the first aspect of the present invention.

15 The ruthenium compound to be supported on the carrier may be the same as those exemplified in connection with the catalyst (3) of the first aspect of the present invention. Preferred examples of the ruthenium compound include ruthenium halides, for example, ruthenium chlorides such as RuCl_3 , RuCl_3 hydrate, etc., and ruthenium bromides such as RuBr_3 , RuBr_3 hydrate, etc. More preferably, ruthenium
20 chloride hydrate is used.

 The process for supporting the ruthenium compound on the carrier includes an impregnation process, an equilibrium adsorption process, etc.

25 The calcination is preferably carried out in an air. A weight ratio of ruthenium oxide to the carrier is

preferably from 0.1:99.9 to 20.0:80.0, more preferably from 0.5:99.5 to 15.0:85.0, in particular from 1.0:99.0 to 15.0:85.0.

5 When the ratio of ruthenium oxide is too low, the activity of the produced catalyst may decrease. When the ratio of ruthenium oxide is too high, the cost of the catalyst may increase.

Ruthenium oxide is preferably ruthenium dioxide. Alternatively, ruthenium hydroxide may be used as a precursor of ruthenium oxide.

10 In one preferable embodiment of the process (4) of the second aspect, the catalyst is prepared by a process comprising the steps of:

supporting a ruthenium halide on a carrier,
15 and

calcining the supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

20 As the ruthenium halides, those exemplified in the above may be used. Among them, ruthenium chlorides such as RuCl_3 , RuCl_3 hydrate and ruthenium bromide such as RuBr_3 , RuBr_3 hydrate are preferred. In particular, ruthenium chloride hydrate is preferred.

25 In the calcining step, the ruthenium halide-supported

one, which is obtained in the previous ruthenium halide-supporting step, is calcined at a temperature of at least 200°C in an atmosphere selected from the group consisting
5 an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

Examples of the inert gas include nitrogen, helium, etc. Examples of the oxidizing gas include air, oxygen, a mixture of nitrogen and oxygen, etc. Examples of the
10 reducing gas include hydrogen, a mixture of hydrogen and nitrogen, etc. Among them, the air is preferable.

Preferably, the ruthenium halide-supported one is calcined and oxidized in the atmosphere containing oxygen to form supported ruthenium oxide having a higher activity. The atmosphere containing oxygen is usually the air.

15 The calcination temperature is preferably from 250 to 600°C, more preferably from 250 to 450°C, particularly preferably from 250 to 400°C. When the calcination temperature is too low, a large amount of ruthenium compound remains unoxidized and thus the obtained catalyst
20 may have an insufficient activity. When the calcination temperature is too high, the ruthenium oxide particles tend to agglomerate, so that the catalytic activity deteriorates.

The calcination time is preferably from 30 minutes to 10 hours.

25 Preferably, substantially all the particles, which are

generated in the oxidizing step are converted to ruthenium oxide, although some particles may remain unconverted insofar as the effects of the present invention are not impaired.

5 Hereinafter, a reaction process for producing chlorine by oxidizing hydrogen chloride using Catalyst b to measure B(b) is explained.

10 As a material of a test reaction tube, nickel, glass, quartz glass, and the like can be used. Since feed gasses and formed gasses are corrosive, some special cares should be taken when other material is used. When the catalysts a and b to be filled in the reactor tube have a high activity, the heat of reaction cannot be removed from the reaction tube. In such a case, each catalyst is diluted with a
15 carrier such as α -alumina balls and then filled in the reaction tube to increase the heat-removing efficiency. When the heat conductivity of the catalyst layers in the reactor tube is insufficient, the heat of reaction is not removed and thus the temperature locally rises and the
20 reaction temperature may not be suitably controlled so that the correct test may not be performed. The temperature of a hot spot set in the Catalyst b layer should be $360 \pm 1^\circ\text{C}$. In general, a temperature distribution is formed in the catalyst a layer and the catalyst b layer. Thus, the
25 temperature in each catalyst layer is from 320 to 360°C

during the reaction. When the reaction temperature is too high, RuO_2 , which is a catalytically active site, quickly agglomerates, and therefore $B(b)$ may not be measured correctly. When the reaction temperature is too low, RuO_2 , which is a catalytically active site, slowly agglomerates, and thus $B(b)$ may not be measured correctly. When the reaction is carried out by taking the above points into account, the test results can be obtained with good reproducibility.

In the preferable supported ruthenium oxide catalyst, the peak intensity ratios $A(b)$ and $B(b)$ satisfy the following equation:

$$1 \leq B(b)/A(b) \leq 1.45$$

in which $A(b)$ and $B(b)$ are the same as defined in the above explanation of the measuring by the EXAFS method. As already described, it has been found that the above peak intensity ratio has the relationship with the structure of ruthenium oxide supported on the carrier. In addition, it has been found that the stability of the peak intensity ratio, which is represented by $B(b)/A(b)$, correlates with the stability of the catalytic activity, wherein $A(b)$, $B(b)$ are the peak intensity ratios measured by the EXAFS method as already described above.

That is, the sintering of ruthenium dioxide in the catalyst is less, as the $B(b)/A(b)$ is smaller.

In the case of the catalyst (3) of the first aspect of the present invention, the catalyst is obtained by main four preparation processes comprising the steps of: supporting process, calcining process, hydrazine-treating process and oxidizing process. In addition to these four process, alkali metal chloride-adding process, washing process and drying process were added to the catalyst preparation process resulted in establishing the catalyst preparation process which has many processes. From the viewpoint of the convenient preparation of catalysts, a process comprising the steps of supporting process and calcining process is very short catalyst preparation process which is comprised by two processes. The above process is preferred because the time of catalyst preparation is short and a preparation cost decrease. Moreover, the above catalysts were more active than the catalyst which was prepared by oxidizing the ruthenium catalyst prepared by hydrogenation of supported ruthenium chloride on a carrier by hydrogen.

Next, the process (5) of the second aspect of the present invention is explained. This process comprises the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide carrier containing the rutile crystal form,
and

calcining said supported one at a temperature of 200°C to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere.

5 In one preferred embodiment of the process (5), the catalyst is prepared by a process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a carrier,
and

10 calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst
15 after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively C(b) and D(b), and which satisfy the following equation (2):

$$0.79 \leq D(b)/C(b) \leq 1 \quad (2)$$

20 provided that $C(b) \geq 3.0 \times 10^{-4}$ mol/min·g-cat
wherein C(b) is a catalytic activity value of the produced catalyst b, which is measured by the catalytic activity test and D(b) is a catalytic activity value of the catalyst b, which is measured by the catalytic activity test after a
25 50 hours reaction test;

in which

the 50 hours reaction test is carried out by filling supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical α -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min.,

respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot) at 300±1°C, after 2.0±1.0 hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =

Amount of chlorine gas from reactor exit (mol/min.) / catalyst weight (g).

Hereinafter, the concrete procedures of the process (5) of the second aspect of the present invention will be explained.

The ruthenium compound may be supported on the carrier by the same supporting method as that explained in connection with the processes (3) and (4) of the second aspect of the present invention. The carrier may be a titanium oxide carrier containing the rutile crystal, which is explained in connection with the catalyst (1) of the

first aspect of the present invention.

The calcination step may be carried out in the same way as that explained in connection with the process (4) of the second aspect of the present invention. That is, this
5 process is characterized in that the ruthenium compound-supported one is calcined at a temperature of 200 to 600°C and carried out in an oxidizing gas atmosphere, an inert gas atmosphere or a reducing gas atmosphere.

The preferable calcination temperature may be the same
10 as that explained in connection with the process (4) of the second aspect of the present invention.

The catalyst prepared by the process (5) is characterized in that it suffers from less deactivation in the catalytic activity test when the 50 hours reaction test
15 is carried out at a temperature of $360 \pm 1^\circ\text{C}$. That is, the $D(b)/C(b)$ ratio, which is defined in the above, is at least 0.79, preferably at least 0.81, more preferably at least 0.84.

$C(b)$ is usually at least 3.0, preferably at least 3.5.

20 The supported ruthenium oxide catalyst prepared by the process (4) has a high catalytic activity.

The process (6) of the second aspect of the present invention comprises the following steps but neither a calcining step nor a treating step with hydrazine:

25 supporting a ruthenium halide on a titanium oxide

carrier containing the rutile crystal form,
and

drying said supported one in an atmosphere selected
from the group consisting of an oxidizing gas atmosphere,
5 an inert gas atmosphere and a reducing gas atmosphere at a
temperature of 20°C to less than 200°C.

In one preferable embodiment of the process (6) of the
second aspect of the present invention, the catalyst is
prepared by a process comprising the following steps but
10 neither a calcining step nor a treating step with
hydrazine:

supporting a ruthenium halide on a titanium oxide
carrier containing the rutile crystal form,
and

15 drying said supported one in an atmosphere selected
from the group consisting of an oxidizing gas atmosphere,
an inert gas atmosphere and a reducing gas atmosphere at a
temperature of 20°C to less than 200°C,
wherein the catalytic activity value of the produced
20 catalyst and the catalytic activity value of the catalyst
after 50 hours reaction test, which are measured by a
catalytic activity test which is defined below, are
respectively E(b) and F(b), and which satisfy the following
equation (3);

25
$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$

provided that $E(b) \geq 3.0 \times 10^{-4}$ mol/min.g-cat.,
in which

50 Hours reaction test: Supported ruthenium oxide
Catalysts a and b are filled in a reactor in this order
5 from the inlet of the reactor in a weight ratio of 1:10
(Catalyst a to Catalyst b), and a hydrogen chloride gas is
supplied under atmospheric pressure at a flow rate of 0.185
to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a
flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the
10 reaction for 50 hours while maintaining the hot spot of
Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, in which Catalyst a is a supported
ruthenium oxide catalyst having a chlorine formation
activity per unit mass of the catalyst of 2×10^{-4} to $3 \times$
 10^{-4} mol/min.g-cat., which is obtained in a reaction test
15 for forming chlorine by oxidizing hydrogen chloride with
oxygen at 300°C with a molar ratio of hydrogen chloride to
oxygen being 1:1, and Catalyst b is a supported ruthenium
oxide catalyst produced by the above process,
and in which

20 Catalytic activity test: 2.3 to 2.5 grams of a
catalyst is diluted by mixing with 10 to 20 g of a
spherical α -alumina carrier having a diameter of 2 mm, and
filled in a quartz reactor tube having an inner diameter of
12 mm, then a hydrogen chloride gas and an oxygen gas are
25 supplied in the reactor under atmospheric pressure at flow

rates of 190 to 210 ml/min. and 190 to 210 ml/min.
 respectively (both volumes being converted to those at 0°C
 under 101 kPa) while heating the reactor in an electric
 furnace and maintaining the internal temperature (hot spot)
 5 at $300 \pm 1^\circ\text{C}$, after 2.0 ± 1.0 hours from the start of the
 reaction, an exit gas from the reactor is sampled by
 passing it through a 30 mass % aqueous solution of
 potassium iodide, the amount of formed chlorine and the
 amount of unreacted hydrogen chloride are measured by an
 10 iodine titration method and a neutralization titration
 method, respectively, and thereafter a chlorine formation
 activity per unit mass of the catalyst is calculated by the
 following equation and used as a catalyst activity:
 Chlorine formation activity per unit mass of the catalyst
 15 (mol/min.g-cat.) =

$$\frac{\text{Amount of chlorine gas from reactor exit (mol/min.)}}{\text{catalyst weight (g)}}$$

The catalyst prepared by the process (6) is
 characterized in that it suffers from less deactivation in
 20 the catalytic activity test when the 50 hours reaction test
 is carried out at a temperature of $360 \pm 1^\circ\text{C}$. That is, the
 $F(b)/E(b)$ ratio, which is defined in the above, is at least
 0.80, preferably at least 0.83, more preferably at least
 0.85.

25 $E(b)$ is usually at least 3.0, preferably at least 3.5.

Hereinafter, the concrete procedures of the process (6) of the second aspect of the present invention will be explained.

5 Firstly, the step to support the ruthenium halide on the carrier is explained. The carrier may be the same as that exemplified in connection with the catalyst (1) of the first aspect of the present invention. That is, titanium oxide containing rutile crystalline titanium oxide, which is preferably used in the present invention, means titanium
10 oxide containing the rutile crystal, when the ratio of the rutile crystal to the anatase crystal in titanium oxide is measured by the X-ray diffraction analysis. This analysis is explained in connection with the catalyst (1) of the first aspect of the present invention.

15 Titanium oxide should contain the rutile crystal. The proportion of the rutile crystal is preferably at least 10 %, more preferably at least 30 %, in particular at least 80 %.

20 As the ruthenium halides, those exemplified in the connection with the catalyst (3) of the first aspect of the present invention may be used. Preferable examples of the ruthenium halides include ruthenium chlorides such as RuCl_3 , RuCl_3 hydrate; ruthenium bromide such as RuBr_3 , RuBr_3 hydrate; and ruthenium oxychlorides such as Ru_2OCl_4 , Ru_2OCl_5 .
25 In particular, ruthenium chloride hydrate is preferred.

That is, in the present invention, ruthenium (III) chloride, ruthenium (III) chloride hydrate or a compound obtained by dissolving ruthenium (III) chloride hydrate in water and spontaneously hydrolyzing it may be used. Furthermore,
5 ruthenium (III) bromide, ruthenium (III) bromide hydrate or a compound obtained by dissolving ruthenium (III) bromide hydrate in water and spontaneously hydrolyzing it may be used. More preferably, ruthenium chloride hydrate is used.

The process for supporting the ruthenium halide on the
10 carrier includes an impregnation process, an equilibrium adsorption process, etc.

The carrier supporting the ruthenium halide is dried under air or nitrogen.

A weight ratio of ruthenium oxide to the carrier is
15 preferably from 0.15:99.85 to 31.2:68.8, more preferably from 0.8:99.2 to 23.4:76.6, particularly preferably from 1.6:98.4 to 23.4:76.6. When the ratio of ruthenium halide is too low, the activity of the produced catalyst may decrease. When the ratio of ruthenium halide is too high,
20 the cost of the catalyst may increase.

In the drying step, the carrier supporting the ruthenium halide is dried at a temperature of 20 to 200°C in an oxidizing gas atmosphere, an inert gas atmosphere or a reducing gas atmosphere. Examples of the inert gas
25 include nitrogen, helium, etc. Examples of the oxidizing

gas include air, oxygen, a mixture of nitrogen and oxygen, etc. Examples of the reducing gas include hydrogen, a mixture of hydrogen and nitrogen, etc. Preferably, the drying is carried out in the air or nitrogen.

5 The drying temperature is preferably from 25 to 200°C, more preferably from 60 to 200°C, particularly preferably from 60 to 150°C. The drying temperature is maintained in a specific range, since a part of the ruthenium halide is converted to ruthenium oxide as the drying temperature
10 rises. When the drying temperature is too low, most of water is not evaporated and remains on the carrier, and thus the handling of the catalyst may become difficult. When the drying temperature is too high, a part of the ruthenium halide is converted to ruthenium oxide.

15 The drying time is preferably from 30 minutes to 10 hours.

Hereinafter, a reaction process for producing chlorine by oxidizing hydrogen chloride using Catalyst b to measure F(b) is explained.

20 As a material of a test reaction tube, nickel, glass, quartz glass, and the like can be used. Since reaction gasses and formed gasses are corrosive, some special cares should be taken when other material is used. When the catalysts a and b to be filled in the reactor tube have a
25 high activity, the heat of reaction cannot be removed from

the reaction tube. In such a case, each catalyst is diluted with a carrier such as α -alumina balls and then filled in the reaction tube to increase the heat-removing efficiency. When the heat conductivity of the catalyst layers in the reactor tube is insufficient, the heat of reaction is not removed and thus the temperature locally rises and the reaction temperature may not be suitably controlled so that the correct test may not be performed. The temperature of a hot spot set in the Catalyst b layer should be $360 \pm 1^\circ\text{C}$. In general, a temperature distribution is formed in the catalyst a layer and the catalyst b layer. Thus, the temperature in each catalyst layer is from 320 to 360°C during the reaction. When the reaction temperature is too high, the ruthenium compound, which is a catalytically active site, quickly agglomerates, and therefore F(b) may not be measured correctly. When the reaction temperature is too low, the ruthenium compound, which is a catalytically active site, slowly agglomerates, and thus F(b) may not be measured correctly. When the reaction is carried out by taking the above points into account, the test results can be obtained with good reproducibility.

In the case of the catalyst (3) of the first aspect of the present invention, the catalyst is obtained by main four preparation processes comprising the steps of:

supporting process, calcining process, hydrazine-treating process and oxidizing process. In addition to these four process, alkali metal chloride-adding process, washing process and drying process were added to the catalyst preparation process resulted in establishing the catalyst preparation process which has many processes. From the viewpoint of convenient preparation of catalysts, a process comprising the steps of: supporting process and drying process is very short catalyst preparation process which is comprised by two processes. The above process is preferred because the time of catalyst preparation is short and a preparation cost decrease. Moreover, the above catalysts were more active than the catalyst which was prepared by oxidizing the ruthenium catalyst prepared by hydrogenation of supported ruthenium chloride on a carrier by hydrogen.

The supported ruthenium oxide catalyst and the supported ruthenium chloride catalyst have a high catalytic activity.

The third aspect of the present invention relates to a process for producing chlorine by oxidizing hydrogen chloride with oxygen, which uses at least one catalyst selected from the group consisting of the following catalysts (1) to (6):

(1) a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and

which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and
conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,
calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,
and

oxidizing said hydrazine-treated one;

(4) a supported ruthenium oxide catalyst produced by a process comprising the steps of:

supporting a ruthenium compound on a carrier,

and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein, when the peak intensity ratio of the produced catalyst and that of the catalyst after a 50 hours reaction test, which are measured by an extended X-ray absorption fine structure analysis (EXAFS) method, are A(b) and B(b) respectively, the peak intensity ratios A(b) and B(b) satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that $A(b) \leq 0.8$,

wherein A(b) is a peak intensity ratio of as-produced Catalyst b measured by the EXAFS method, and B(b) is a peak intensity ratio of Catalyst b measured by the EXAFS method after the 50 hours reaction test; in which

50 Hours reaction test: Supported ruthenium oxide Catalysts a and b are filled in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of

Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a supported ruthenium oxide catalyst produced by a process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide

carrier containing the rutile form,
and

calcining said supported one at a temperature of 200°C
to 600°C in an atmosphere selected from the group
5 consisting of an oxidizing gas atmosphere, an inert gas
atmosphere and a reducing gas atmosphere;
and

(6) a supported ruthenium oxide catalyst produced by a
process comprising the following steps but neither a
10 calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide
carrier containing the rutile crystal form,
and

drying said supported one in an atmosphere selected
15 from the group consisting of an oxidizing gas atmosphere,
an inert gas atmosphere and a reducing gas atmosphere at a
temperature of 20°C to less than 200°C.

The catalysts used in the above process for producing
chlorine according to the third aspect of the present
20 invention are already described in connection with the
first and second aspects of the present invention. For
example, the catalyst (1) used in the third aspect is
described in connection with the catalyst (1) of the first
aspect. The catalyst (2) used in the third aspect is
25 described in connection with the catalyst (2) of the first

aspect. The catalyst (3) used in the third aspect is described in connection with the catalyst (3) of the first aspect. The catalyst (4) used in the third aspect is described in connection with the catalyst (4) prepared by the process of the second aspect. The catalyst (5) used in the third aspect is described in connection with the catalyst (5) prepared by the process of the second aspect. The catalyst (6) used in the third aspect is described in connection with the catalyst (6) prepared by the process of the second aspect.

One preferable example of the catalyst (5) used in the process of third aspect of the present invention is a catalyst which is produced by a process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a carrier,
and

calcining said supported one at a temperature of 200°C to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively C(b) and D(b), and which satisfy the following equation (2):

$$0.79 \leq D(b)/C(b) \leq 1 \quad (2)$$

provided that $C(b) \geq 3.0 \times 10^{-4}$ mol/min.g-cat.

wherein $C(b)$ is a catalytic activity value of the produced catalyst b, which is measured by the catalytic activity test and $D(b)$ is a catalytic activity value of the catalyst b, which is measured by the catalytic activity test after a 50 hours reaction test;
in which

the 50 hours reaction test is carried out by filling supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process,
and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical α -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot) at $300 \pm 1^\circ\text{C}$, after 2.0 ± 1.0 hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

$$\begin{aligned} &\text{Chlorine formation activity per unit mass of the catalyst} \\ &(\text{mol/min.g-cat.}) = \\ &\frac{\text{Amount of chlorine gas from reactor exit (mol/min.)}}{\text{catalyst weight (g)}}. \end{aligned}$$

The preferable example of the catalyst (5) used in the process of the third aspect of the present invention is

already explained in connection with the preferable example of the catalyst (5) prepared by the process of the second aspect of the present invention.

One preferable example of the catalyst (6) used in the
5 process of third aspect of the present invention is a catalyst which is produced by a process comprising the following steps but neither a calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide
10 carrier containing the rutile crystal form,
and

drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a
15 temperature of 20°C to less than 200°C,
wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test , which are measured by a catalytic activity test which is defined below, are
20 respectively E(b) and F(b), and which satisfy the following equation (3):

$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$

provided that $E(b) \geq 3.0 \times 10^{-4}$ mol/min.g-cat.

in which

25 50 Hours reaction test: Supported ruthenium oxide

Catalysts a and b are filled in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical α -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric

furnace and maintaining the internal temperature (hot spot) at $300 \pm 1^\circ\text{C}$, after 2.0 ± 1.0 hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

$$\text{Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.)} = \frac{\text{Amount of chlorine gas from reactor exit (mol/min.)}}{\text{catalyst weight (g).}}$$

The preferable example of the catalyst (6) used in the process of the third aspect of the present invention is already explained in connection with the preferable example of the catalyst (6) prepared by the process of the second aspect of the present invention.

The process of the third aspect of the present invention produces chlorine by oxidizing hydrogen chloride with oxygen in the presence of one or more of the above catalysts (1) to (6). In this process, the reaction system includes, for example, a flow system such as a fixed bed system or a fluidized bed system. Preferably, a gas phase

fixed bed flow system and a gas phase fluidized bed flow system are used. The fixed bed system has an advantage that no separation of the reaction gas from the catalyst is required and that a high conversion can be accomplished because the raw gas can be sufficiently contacted with the catalyst. The fluidized bed system has an advantage that heat in the reactor can be sufficiently removed and the temperature distribution range in the reactor can be minimized.

When the reaction temperature is high, ruthenium oxide in a highly oxidized state may be volatilized. Thus, the oxidation reaction is preferably conducted at a relatively low temperature, preferably, at a temperature of from 100 to 500°C, more preferably from 200 to 380°C.

The reaction pressure is usually from atmospheric pressure to about 5.07 MPa.

As a source of oxygen gas, an air as such or pure oxygen may be used. Since other components may be discharged out of the plant at the same time as the discharge of inert nitrogen gas, pure oxygen is containing no inert gas is preferably used.

A theoretical molar amount of oxygen based on hydrogen chloride is 1/4 mole, but oxygen is usually fed in an amount of 0.1 to 10 times larger than the theoretical amount.

In the case of the fixed bed gas phase flow system, the amount of the catalyst is usually from about 10 to 20,000 hr⁻¹ in terms of a ratio (GHSV) to a feed rate of hydrogen chloride as the raw material under atmospheric pressure. GHSV means a Gas Hourly Space Velocity, which is a ratio of a volume of fed hydrogen chloride (liter/hr.) to a volume of the catalyst (liters).

Example 1

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (50.0 g), pure water (35.3 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (6.6 g) were added and kneaded.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide (49.1 g).

The above operation was repeated, and white noodle-form titanium oxide (105.0 g in total) was obtained.

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 2 hours and calcined at the same temperature (700°C) for 3 hours to obtain white noodle-form titanium oxide (102.3 g).

After calcination, the noodle-form solid was cut to a

length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (100.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (12.75 g) dissolved in pure water (42.5 g), and dried at 60°C for 2 hours.

Then, 21.6g of this solid from the obtained one was heated under air from room temperature to 200°C over 1 hour and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (13.3 g), pure water (120 g) and hydrazine monohydrate (3.20 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 155 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated eight times. The pH of the first wash liquid was 11.4, and that of the eighth wash liquid was 7.4.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same
5 temperature for 3 hours to obtain the black solid (20.9 g).

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated six times. Thereafter, an aqueous solution of
10 silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (20.6 g).

15 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 5.9 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 4.5 \text{ mass } \%$$

20 Next, the adsorbed amount of carbon monoxide was measured by metal surface area measuring method (MSA).

The catalyst (0.1 g) was sampled and the adsorbed amount of carbon monoxide was measured under the following conditions:

25 -Apparatus: Full automatic apparatus for measuring gas

adsorption on catalysts R 6015 (manufactured by OKURA
RIKEN)

-Hydrogen flow rate: 50 ml/min.

-Heating rate: 20°C/min.

5 -Reducing conditions: 220°C, 60 minutes

-Helium purging: He 50 ml/min, 5 minutes

-Cooling rate: 25°C/min.

-Carbon monoxide adsorption: Carbon monoxide being adsorbed
on the catalyst by pulse injecting carbon monoxide (each
10 0.45 ml) several times at 50°C with flowing helium at 50
ml/min.

The measurement was carried out twice. The averaged
adsorbed amount of carbon monoxide was 4.42 ml/g-cat., and
the adsorbed amount per unit mass of ruthenium was 98.2
15 ml/g-Ru.

The obtained ruthenium oxide catalyst supported on
titanium oxide (2.5 g) was diluted by mixing with a
commercially available spherical α -alumina carrier having a
diameter of 2 mm (SSA 995 manufactured by NIKKATO Co.,
20 Ltd.) (10 g) to dilute the catalyst, and then charged in a
quartz reactor tube having an inner diameter of 12 mm. To
the reactor tube, hydrogen chloride gas and oxygen gas were
supplied at flow rates of 192 ml/min. and 192 ml/min.,
respectively (each converted to a volume at 0°C under 1
25 atm.)

The quartz reactor tube was heated in an electric furnace to adjust the internal temperature (hot spot) to 300°C.

When 2 hours after the start of the reaction, the gas from the exit of the reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively.

The chlorine formation activity per unit mass of the catalyst, which was calculated according to the following equation, was 11.0×10^{-4} mol/min.g-cat.:

Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =

Amount of exit chlorine formed per unit time (mol/min.) / weight of catalyst (g)

Example 2

A reaction was carried out in the same manner as that in Example 1 except that the catalyst prepared in Example 1 (1.0 g) was diluted by mixing with a commercially available spherical α -alumina carrier having a diameter of 2 mm (20 g) to dilute the catalyst, and then charged in the quartz reactor tube, and the oxygen gas was supplied at a flow rate of 206 ml/min.

When 2.4 hours after the start of the reaction, the

chlorine formation activity per unit mass of the catalyst was 25.5×10^{-4} mol/min.g-cat.

Example 3

A catalyst was prepared as follows.

5 To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (50.0 g), pure water (35.3 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (6.6 g) were added and kneaded.

10 The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide.

The above operation was repeated, and white noodle-form titanium oxide (94.9 g in total) was obtained.

15 The obtained titanium oxide solid was heated under air from room temperature to 700°C over 2 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide.

20 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl₃.nH₂O, ruthenium content: 38.2 mass %) (2.49

g) dissolved in pure water (8.5 g), dried at room temperature overnight, and further dried at 60°C for 2 hours.

5 The obtained solid (22.4 g) was heated under air from room temperature to 300°C over 1.5 hours while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours.

10 The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (13.2 g), pure water (120 g) and hydrazine monohydrate (3.20 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 155 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30
15 minutes, followed by filtration. The washing and filtration were repeated seven times. The pH of the first wash liquid was 10.5, and that of the seventh wash liquid was 8.0.

20 To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

25 Then, the black solid was heated under air from room

temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the black solid (21.3 g).

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by
5 recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to
10 obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (21.1 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 5.9 \text{ mass \%}$$

15 The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 4.5 \text{ mass \%}$$

The obtained ruthenium oxide catalyst supported on titanium oxide (1.0 g) was diluted by mixing with a commercially available spherical α -alumina carrier having a
20 diameter of 2 mm (20 g) to dilute the catalyst, and charged in the quartz reactor tube. Then, the reaction was carried out in the same manner as that in Example 1 except that the oxygen was supplied at a flow rate of 206 ml/min.

When 2.0 hours after the start of the reaction, the
25 chlorine formation activity per unit mass of the catalyst

was 22.8×10^{-4} mol/min.g-cat.

Example 4

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal)
5 manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g)
and aluminum oxide powder (AES-12 manufactured by Sumitomo
Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the
mixture, pure water (19.0 g) and titanium oxide sol (CSB
(TiO₂ content: 38 mass %) manufactured by Sakai Chemical
10 Industry Co., Ltd.) (7.9 g) were added and kneaded. To the
kneaded mixture, pure water (0.6 g) was added and further
kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of
noodles having a diameter of 1.5 mm ϕ , and dried under air
15 at 60°C for 2 hours to obtain white noodle-form titanium
oxide- α -alumina.

The obtained white noodle-form titanium oxide- α -
alumina was heated under air from room temperature to 600°C
over 1.7 hours and calcined at the same temperature for 3
20 hours to obtain white noodle-form titanium oxide- α -alumina
(50.8 g).

After calcination, the noodle-form solid was cut to a
length of about 5 mm to obtain an extruded white titanium
oxide- α -alumina carrier.

25 Then, the carrier (20.0 g) was impregnated with an

aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (1.63 g) dissolved in pure water (6.1 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

5 The obtained solid was heated under air from room temperature to 250°C over 1.25 hours and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.5 g), pure water (120 g) and hydrazine monohydrate (2.05 g). Bubbling
10 was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were
15 repeated seven times. The pH of the first wash liquid was 10.9, and that of the seventh wash liquid was 7.2.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred,
20 followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room
25 temperature to 350°C over 1 hour and calcined at the same

temperature for 3 hours to obtain the black solid.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation
 5 was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported
 10 on titanium oxide- α -alumina (20.7 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.9 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$15 \quad [\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.0 \text{ mass } \%$$

The obtained ruthenium oxide catalyst supported on titanium oxide- α -alumina (2.5 g) was charged in the quartz reactor tube, and the reaction was carried out in the same manner as that in Example 1 except that the internal
 20 temperature (hot spot) was 301°C.

When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 9.1×10^{-4} mol/min.g-cat.

Example 5

25 A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (20.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (20.0 g) were thoroughly mixed. To the
5 mixture, pure water (14.6 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (5.26 g) were added and kneaded, and further kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of
10 noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina.

The obtained white noodle-form solid was heated under air from room temperature to 600°C over 1.7 hours and
15 calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (33.0 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

20 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl₃.nH₂O, ruthenium content: 38.2 mass %) (1.63 g) dissolved in pure water (5.9 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

25 The obtained solid was heated from room temperature to

200°C over 1 hour while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours.

5 The calcined solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.5 g), pure water (120 g) and hydrazine monohydrate (2.05 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the
10 recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 10.4, and that of the fifth wash liquid was 7.4.

15 To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid (20.8 g).

20 Then, the black solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the black solid.

25 After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation

was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to
5 obtain an extruded black ruthenium oxide catalyst supported on titanium oxide- α -alumina (20.5 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3)] \times 100 = 3.9 \text{ mass } \%$$

10 The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.0 \text{ mass } \%$$

Next, the adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The
15 averaged adsorbed amount of carbon monoxide was 2.98 ml/g-cat., and the adsorbed amount per unit mass of ruthenium was 99.3 ml/g-Ru.

The obtained ruthenium oxide catalyst supported on titanium oxide- α -alumina (2.5 g) was charged in the quartz
20 reactor tube and the reaction was carried out in the same manners as those in Example 1 except that the oxygen gas was supplied under atmospheric pressure at a flow rate of 206 ml/l.

When 2.0 hours after the start of the reaction, the
25 chlorine formation activity per unit mass of the catalyst

was 9.1×10^{-4} mol/min.g-cat.

Example 6

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal)
5 manufactured by Sakai Chemical Industry Co., Ltd.) (30.1 g)
and aluminum oxide powder (AES-12 manufactured by Sumitomo
Chemical Co., Ltd.) (60.0 g) were thoroughly mixed. To the
mixture, pure water (20.3 g) and titanium oxide sol (CSB
10 (TiO₂ content: 38 mass %) manufactured by Sakai Chemical
Industry Co., Ltd.) (11.9 g) were added and kneaded, and
further kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of
noodles having a diameter of 1.5 mm ϕ , and dried under air
at 60°C for 4 hours to obtain white noodle-form titanium
15 oxide- α -alumina.

Then, 55.5g of this solid from the obtained white
noodle-form one was heated under air from room temperature
to 600°C over 1.7 hours and calcined at the same
temperature for 3 hours to obtain white noodle-form
20 titanium oxide- α -alumina (53.8 g).

After calcination, the noodle-form solid was cut to a
length of about 5 mm to obtain an extruded white titanium
oxide- α -alumina carrier.

Then, the carrier (20.0 g) was impregnated with an
25 aqueous solution of commercially available ruthenium

chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (0.82 g) dissolved in pure water (4.49 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

The obtained solid was heated from room temperature to
5 200°C over 1 hour while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours.

The calcined solid was dipped in a solution containing
2N aqueous solution of potassium hydroxide (4.2 g), pure
10 water (120 g) and hydrazine monohydrate (1.03 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes,
15 followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 10.6, and that of the fifth wash liquid was 7.3.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred,
20 followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room
25 temperature to 350°C over 1 hour and calcined at the same

temperature for 3 hours to obtain the black solid.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation
5 was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported
10 on titanium oxide- α -alumina (20.2 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.0 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

15
$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.53 \text{ mass } \%$$

Next, the adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The averaged adsorbed amount of carbon monoxide was 1.73 ml/g-cat., and the adsorbed amount per unit mass of ruthenium
20 was 113.1 ml/g-Ru.

The obtained ruthenium oxide catalyst supported on titanium oxide- α -alumina (2.5 g) was charged in the quartz reactor tube and the reaction was carried out in the same
25 manners as those in Example 1.

When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 5.35×10^{-4} mol/min.g-cat.

Example 7

5 A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (120 g) was heated at a heating rate of 6°C/min., and then calcined at 600°C for 3 hours to obtain titanium oxide powder (118.8 g). To this calcined titanium oxide powder (50.0 g), pure water (35.0 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (6.6 g) were added and kneaded.

15 The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide (42.2 g).

The obtained titanium oxide solid was heated under air from room temperature to 350°C over 1 hour and calcined at 350°C for 3 hours, and further heated at a heating rate of 6°C/min. and calcined at 500°C for 3 hours to obtain white noodle-form titanium oxide (42.0 g).

25 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (2.55 g) dissolved in pure water (7.6 g), and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (13.2 g), pure water (120 g) and hydrazine monohydrate (3.20 g). Bubbling was observed as soon as the solid was dipped in the solution. After 60 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.0, and that of the fifth wash liquid was 6.0.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid.

Then, the black solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the black solid (21.2 g).

After calcination, pure water (500 ml) was added to

the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (20.4 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 5.9 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 4.5 \text{ mass \%}$$

Next, the adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The averaged adsorbed amount of carbon monoxide was 3.28 ml/g-cat., and the adsorbed amount per unit mass of ruthenium was 72.9 ml/g-Ru.

Example 8

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (40.1 g) and α -alumina powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (40.0 g) were thoroughly mixed. To the

mixture, the mixed solution of titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) and pure water (31.0 g) was added and kneaded.

5 This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina.

10 The obtained white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 600°C over 1.6 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (75.4 g).

15 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier. The same carrier was prepared by the same method as above, and two portions of the prepared carrier were combined.

20 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl₃.nH₂O, ruthenium content: 37.3 mass %) (1.62 g) dissolved in pure water (5.86 g) and dried at 60°C for 2 hours.

25 The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.38 g), pure

water (40 g) and hydrazine monohydrate (2.04 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.7, and that of the fifth wash liquid was 7.0.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid. Furthermore, another two portions of the gray solid were produced by the same method, and three portions were combined.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid. The bluish gray solid was prepared by the same method as above, and two portions of the prepared solid were combined.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution

of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide- α -alumina (124.6 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass } \%$$

The adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The averaged adsorbed amount of carbon monoxide was 2.36 ml/g-cat., and the adsorbed amount per unit mass of ruthenium was 81.4 ml/g-Ru.

Example 9

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and α -alumina powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the mixture, the mixed solution of titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) and pure water (22.0 g) was added and kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina (53.1 g).

5 The obtained white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 800°C over 2.2 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (52.3 g).

10 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

 Then, the carrier (25.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.01 g) dissolved in pure water (6.9 g) and dried at 60°C for 2 hours.

15 The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (5.24 g), pure water (150 g) and hydrazine monohydrate (1.26 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, 20 followed by filtration. The washing and filtration were 25

repeated five times. The pH of the first wash liquid was 9.1, and that of the fifth wash liquid was 6.7.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred,
5 followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid..

Then, the gray solid was heated under air from room
10 temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation
15 was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst
20 supported on titanium oxide- α -alumina (24.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

25

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass } \%$$

The adsorbed amount of carbon monoxide was measured by MSA under the same conditions as those in Example 1. The measurement was carried out twice. The averaged adsorbed amount of carbon monoxide was 1.21 ml/g-cat., and the
5 adsorbed amount per unit mass of ruthenium was 80.7 ml/g-Ru.

Example 10

1) The first catalyst of this Example was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile
10 crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.1 g), pure water (42.1 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added and kneaded. A dry
15 air was blown onto the kneaded mixture at room temperature to dry the mixture until an adequate viscosity was reached. The decreased amount of water by drying was 0.5 g.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium
20 oxide (54.0 g).

Then, 27.3g of this solid from the obtained titanium oxide one was heated under air from room temperature to 800°C over 2 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide (26.7 g).

25 After calcination, the noodle-form solid was cut to a

length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.61 g) dissolved in pure water (10.2 g), and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (8.34 g), pure water (121 g) and hydrazine monohydrate (2.02 g). Bubbling was observed as soon as the dried solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 8.9, and that of the fifth wash liquid was 5.7.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same

temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same
5 operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst
10 supported on titanium oxide (20.6 g).

A packing density of the obtained catalyst was measured by packing the catalyst in a 50 ml graduated cylinder, and calculated from a packing weight and a packing volume according to the following equation:
15
$$\text{Packing density} = \text{Packing weight} / \text{Packing volume}$$

The packing density was 0.91 g/ml.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 3.8 \text{ mass } \%$$

20 The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 2.9 \text{ mass } \%$$

The obtained catalyst is named "Catalyst c".

2) The second catalyst of this Example was prepared as follows.

25 Titanium oxide powder (STR-60R (100 % rutile crystal)

manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and α -alumina powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the mixture, titanium oxide sol (CSB (TiO_2 content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) and pure water (22.0 g) were added and kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina (53.1 g).

The obtained white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 800°C over 2.2 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (52.3 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

Then, the carrier (25.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.01 g) dissolved in pure water (6.9 g) and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (5.24 g), pure

water (150 g) and hydrazine monohydrate (1.26 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.1, and that of the fifth wash liquid was 6.7.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid (24.8 g).

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to

obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide- α -alumina (20.6 g). The packing density of this catalyst was 1.02 g/ml.

5 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.4 \text{ mass \%}$$

The obtained catalyst was named "Catalyst b".

10 3) The third catalyst of this Example was prepared as follows.

A commercially available α -alumina (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.1 g), ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.62 g), pure water (3.0 g) and alumina sol (ALUMINA SOL 200 manufactured by Nissan Chemical Industries, Ltd.) (8.53 g) were thoroughly mixed. A dry air was blown onto the mixture at room temperature to dry the mixture until an adequate viscosity was reached.

20 This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain brown noodle-form ruthenium oxide- α -alumina.

The obtained brown noodle-form ruthenium oxide- α -alumina was heated under air from room temperature to 350°C

over 1 hour and calcined at the same temperature for 3 hours to obtain gray noodle-form ruthenium oxide catalyst supported on α -alumina (25.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.5 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass } \%$$

The packing density of obtained catalyst was 1.31 g/ml.

The catalyst obtained by the same preparation method which was mentioned above was named "Catalyst a".

4) In a glass test reactor tube having an inner diameter of 15 mm, in which a thermocouple-protective tube having an outer diameter of 6 mm was inserted, above-prepared Catalysts a, b and c were charged in a volume ratio of 2:13:5 (a:b:c) in a reactor in this order from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of α -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts a, b and c were as follows:

Catalyst a: 0.68 ml (0.89 g)

Catalyst b: 4.33 ml (4.42 g)

Catalyst c: 1.69 ml (1.54 g)

The total volume of charged catalysts was 6.7 ml.

The upper zone of the Catalyst layer was formed by the

Catalyst a and the Catalyst b, while the lower zone of the Catalyst layer was formed by the Catalyst c, and each zone was heated in a respective electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and
5 flowed under atmospheric pressure from the upper zone to
the lower zone at flow rates of 50 ml/min. and 25 ml/min.,
respectively (each converted to a volume at 0°C under 101
kPa.) This reaction operation was carried out for 80 hours
under the above conditions while maintaining the conversion
10 of hydrogen chloride at higher than 70 %. After 80 hours,
the internal temperature (hot spot) of the upper zone in
the test reactor tube was 343°C, while that of the lower
zone was 297°C. At this time, the gas from the outlet of
the test reactor tube was sampled by passing it through an
15 aqueous 30 mass % potassium iodide solution, and the amount
of chlorine formed and the amount of unreacted hydrogen
chloride were determined by iodometric titration and
neutralization titration, respectively. The conversion of
hydrogen chloride was 91.2 %.

20 5) Furthermore, the activity of Catalyst c was
measured as follows:

The activity of Catalyst c was represented by $M(c)$.

Catalyst c was isolated from the mixture of Catalyst c
and the α -alumina carrier used in the step 4), and one gram
25 of Catalyst c was thoroughly mixed again with the

commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (4 g) to dilute Catalyst c, and diluted Catalyst c was charged in a quartz reactor tube having an inner diameter of 12 mm.

5 Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 77 ml/min. and 77 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the
10 internal temperature (hot spot) at 299°C. When 2.2 hours after the start of the reaction, the gas from the outlet of the reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen
15 chloride were determined by iodometric titration and neutralization titration, respectively.

The chlorine formation activity per unit mass of the catalyst, which was calculated according to the following equation, was 8.6×10^{-4} mol/min.g-cat.:

20 Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =
Amount of outlet chlorine formed per unit time (mol/min.) /
weight of catalyst (g)

25 6) In this step, the same Catalysts a and c as those used in the step 4) were used. As Catalyst b, one prepared

by the same method as that of the step 2) was used.

In a nickel test reactor tube having an inner diameter of 14 mm, in which a thermocouple-protective tube having an outer diameter of 5 mm was inserted, Catalysts a, b and c were charged in a volume ratio of 2:13:5 (a:b:c) from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of α -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts a, b and c were as follows:

Catalyst a: 1.73 ml (2.27 g)
Catalyst b: 11.13 ml (11.35 g)
Catalyst c: 4.33 ml (3.94 g)

The total volume of charged catalysts was 17.2 ml.

The upper zone of the Catalyst layer was formed by the Catalyst a and the Catalyst b, while the lower zone of the Catalyst layer was formed by the Catalyst c, and each zone was heated in a respective electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 130 ml/min. and 65 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 512 hours under the same conditions while maintaining the conversion of hydrogen chloride at higher than 70 %. After 512 hours, the internal temperature (hot spot) of the upper

zone in the test reactor tube was 352°C, while that of the lower zone was 301°C. At this time, the conversion of hydrogen chloride was 91.1 %.

7) Furthermore, the activity of Catalyst c was
5 measured as follows:

This activity of Catalyst c was represented by $N(c)$.

Catalyst c was isolated from the mixture of Catalyst c and the α -alumina carrier used in the step 6), and 2.5 grams of Catalyst c was thoroughly mixed again with the
10 commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10 g) to dilute Catalyst c, and diluted Catalyst c was charged in a quartz reactor tube having an inner diameter of 12 mm. Then, hydrogen chloride gas and oxygen gas were supplied in
15 the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 192 ml/min., respectively. The quartz reactor tube was heated with an electric furnace to keep the internal temperature (hot spot) at 300°C. When
20 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 7.6×10^{-4} mol/min.g-cat.

Accordingly, the ratio of $N(c)$ to $M(c)$ [$N(c)/M(c)$] was 0.89.

From the above result, it can be seen that Catalyst c
25 had the high catalytic activity, and could produce chlorine

with a smaller amount of the catalyst at a lower temperature. Furthermore, when Catalyst c was used in the above chlorine formation reaction, it had a longer life.

Example 11

5 1) The first catalyst of this Example was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (80.0 g), pure water (64.2 g) and titanium oxide sol (CSB
10 (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) were added and kneaded. A dry air was blown onto the kneaded mixture at room temperature to dry the mixture until an adequate viscosity was reached.

The mixture was molded by extrusion in the form of
15 noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide.

The obtained titanium oxide solid was heated under air from room temperature to 800°C over 2.2 hours and calcined
20 at the same temperature for 3 hours to obtain white noodle-form titanium oxide (72.1 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

25 Then, the carrier (20.0 g) was impregnated with an

aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (2.04 g) dissolved in pure water (8.18 g), and dried at 60°C for 2 hours.

5 The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (10.6 g), pure water (120 g) and hydrazine monohydrate (2.55 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by
10 filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.7, and that of the fifth wash liquid was 5.9.

15 Another two portions of the same solid were prepared by the same method as above, and three portions of the solid were combined.

 To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (150 g) was added, and stirred,
20 followed by recovering of the solid by filtration. The same operation was repeated three times.

 The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

 Then, the gray solid was heated under air from room
25 temperature to 350°C over 1 hour and calcined at the same

temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same
5 operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst
10 supported on titanium oxide (61.6 g).

A packing density of the obtained catalyst was measured and calculated in the same manner as that of Example 10. The packing density was 0.83 g/ml.

The calculated content of ruthenium oxide was as
15 follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 4.8 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 3.6 \text{ mass } \%$$

The obtained catalyst is named "Catalyst d".

20 2) The second catalyst of this Example was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (64.0 g) and α -alumina powder (AES-12 manufactured by Sumitomo
25 Chemical Co., Ltd.) (16.0 g) were thoroughly mixed. To the

mixture, titanium oxide sol (CSB (TiO_2 content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) and pure water (49.3 g) were added and kneaded.

5 This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina.

10 The obtained white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 600°C over 1.6 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (73.9 g).

15 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

20 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (2.03 g) dissolved in pure water (7.9 g) and dried at 60°C for 2 hours.

25 The obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (10.5 g), pure water (120 g) and hydrazine monohydrate (2.55 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by

filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.2, and that of the fifth wash liquid was 5.8. Another two portions of the same solid were prepared by the same method as above, and three portions of the solid were combined.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid (62.4 g).

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid (61.5 g).

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to

obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide- α -alumina (60.6 g). The packing density of this catalyst was 0.89.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 4.8 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.6 \text{ mass } \%$$

The obtained catalyst was named "Catalyst c".

3) The third catalyst of this Example was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (40.1 g) and α -alumina powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (40.0 g) were thoroughly mixed. To the mixture, the mixed solution of titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (10.6 g) and pure water (31.0 g) was added and kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina.

The obtained white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 600°C

over 1.6 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (75.4 g).

After calcination, the noodle-form solid was cut to a
5 length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier. The same carrier was prepared by the same method as above, and two portions of the prepared carrier were combined.

Then, the carrier (20.0 g) was impregnated with an
10 aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.62 g) dissolved in pure water (5.86 g) and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing
15 2N aqueous solution of potassium hydroxide (8.38 g), pure water (40 g) and hydrazine monohydrate (2.04 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the
20 recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.7, and that of the fifth wash liquid was 7.0.

To the filtrated solid, a 0.5 mol/l aqueous solution
25 of potassium chloride (50 g) was added, and stirred,

followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid. Furthermore, another two portions
5 of the gray solid were produced by the same method, and three portions were combined.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.
10 The bluish gray solid was prepared by the same method as above, and two portions of the prepared solid were combined.

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same
15 operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst
20 supported on titanium oxide- α -alumina (124.6 g). The packing density of this catalyst was 1.02 g/ml.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass \%}$$

25 The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass \%}$$

The obtained catalysy is named "Catalyst b".

4) The fourth catalyst of this Example was prepared as follows.

5 A commercially available α -alumina (AES-12
manufactured by Sumitomo Chemical Co., Ltd.) (30.1 g),
ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3
mass %) (1.62 g), pure water (3.0 g) and alumina sol
(ALUMINA SOL 200 manufactured by Nissan Chemical Industries,
10 Ltd.) (8.53 g) were thoroughly mixed. A dry air was blown
onto the mixture at room temperature to dry the mixture
until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of
noodles having a diameter of 1.5 mm ϕ , and dried under air
15 at 60°C for 4 hours to obtain brown noodle-form ruthenium
oxide- α -alumina.

The obtained brown noodle-form ruthenium oxide- α -
alumina was heated under air from room temperature to 350°C
over 1 hour and calcined at the same temperature for 3
20 hours to obtain gray noodle-form ruthenium oxide catalyst
supported on α -alumina (25.8 g).

The calculated content of ruthenium oxide was as
follows:

$$[\text{RuO}_2/(\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.5 \text{ mass \%}$$

25 The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass } \%$$

The obtained catalyst (packing density: 1.31 g/ml) was named "Catalyst a".

5 In a nickel test reactor tube having an inner diameter of 14 mm, in which a thermocouple-protective tube having an outer diameter of 6 mm was inserted, above-prepared Catalysts a, b, c and d were charged in a weight ratio of 10:50:25:25 (a:b:c:d) from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio
10 of α -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts a, b, c and d were as follows:

Catalyst a: 1.73 ml (2.27 g)

Catalyst b: 6.94 ml (7.08 g)

15 Catalyst c: 4.31 ml (3.83 g)

Catalyst d: 4.32 ml (3.58 g)

The total volume of charged catalysts was 17.3 ml.

The upper zone of the Catalyst layer was formed by the Catalyst a, the Catalyst b and the Catalyst c, while the
20 lower zone of the Catalyst layer was formed by the Catalyst d, and each zone was heated in a respective electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper zone to
25 the lower zone at flow rates of 130 ml/min. and 65 ml/min.,

respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 2239 hours while maintaining the conversion of hydrogen chloride at higher than 89 %. After 2239 hours, the internal
5 temperature (hot spot) of the upper zone in the test reactor tube was 367°C, while that of the lower zone was 308°C. At this time, the gas from the outlet of the test reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of
10 chlorine formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively. The conversion of hydrogen chloride was 90.6 %.

5) Furthermore, the activity of Catalyst d was
15 measured as follows:

Catalyst d (2.5 g) was diluted by mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10 g), and diluted Catalyst d was charged in a quartz reactor tube
20 having an inner diameter of 12 mm. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 192 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in
25 an electric furnace to keep the internal temperature (hot

spot) at 300°C. When 2.0 hours after the start of the reaction, the gas from the outlet of the reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine
 5 formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively.

After the following time period from the start of the reaction, a portion of Catalyst d was removed from the
 10 reactor, and the chlorine formation activity per unit mass of Catalyst d was calculated according to the following equation:

Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =

15 Amount of outlet chlorine formed per unit time (mol/min.) / weight of catalyst (g)

The results are as follows:

Initial:	6.9×10^{-4} mol/min.g-cat.
After 502 hours:	5.9×10^{-4} mol/min.g-cat.
20 After 984 hours:	5.1×10^{-4} mol/min.g-cat.
After 1392 hours:	5.4×10^{-4} mol/min.g-cat.
After 1955 hours:	4.7×10^{-4} mol/min.g-cat.
After 2239 hours:	4.8×10^{-4} mol/min.g-cat.

From the above results, it can be seen that Catalyst d
 25 had the high catalytic activity, and could produce chlorine

with a smaller amount of the catalyst at a lower temperature. Furthermore, when Catalyst d was used in the above chlorine formation reaction, it had a longer life.

Example 12

5 1) The first catalyst of this Example was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.8 g) and titanium oxide sol (CSB
10 (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature while drying.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air
15 at 60°C for 4 hours to obtain white noodle-form titanium oxide (58.0 g).

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-
20 form titanium oxide (56.5 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an
25 aqueous solution of commercially available ruthenium

chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (2.39 g) dissolved in pure water (10.4 g), dried at room temperature overnight, and further dried at 60°C for 2 hours.

5 The obtained solid was heated under air from room temperature to 350°C over 1.8 hours while supplying an air at a flow rate of 200 ml/min. and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (20.9 g).

10 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.6 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

15 $[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.3 \text{ mass \%}$

The obtained catalyst is named "Catalyst b".

Measuring method of EXAFS

The EXAFS spectrum at the Ru K absorption edge of Catalyst b was measured with the XAFS spectrometer installed at the Beamline 10B (BL-10B) in the Photon Factory, the Institute of Materials Structure Science, the High Energy Accelerator Research Organization. Using the monochromater employed a Si (311) channel-cut crystal, the intensity of incident X-ray (I0) was measured with a 17 cm ion chamber filled with argon as a gas at room temperature,

20

25

while the intensity of transmitted X-ray (I_t) was measured with a 31 cm ion chamber filled with krypton as a gas at room temperature.

5 In the above measurement, the interval of measuring points and the dwell time for acquiring both signals per one measuring point in each block were as follows:

10 In the first block of the energy (E) of incident X-ray from 21,590 eV to 22,040 eV, the interval was 6.43 eV, and the dwell time was one second at each point (the number of the measuring points was 70).

In the second block of the energy (E) of incident X-ray from 22,040 eV to 22,190 eV, the interval was 1 eV, and the dwell time was one second at each point (the number of the measuring points was 150).

15 In the third block of the energy (E) of incident X-ray from 22,190 eV to 22,590 eV, the interval was 2.5 eV, and the dwell time was two seconds at each point (the number of the measuring points was 160).

20 In the forth block of the energy (E) of incident X-ray from 22,590 eV to 23,190 eV, the interval was 6 eV, and the dwell time was two seconds at each point (the number of the measuring points was 101).

25 The calibration of the energy (E) of incident X-ray was conducted by setting the angle of the monochromater to 24.934 degree at the energy (8980.3 eV) of the pre-edge

peak in the X-ray Absorption Near-Edge Structure (XANES) spectrum of copper metal at the K absorption edge.

Analysis of EXAFS

5 The energy E_0 at the absorption edge of Catalyst b was regarded as 22,123 eV, which is the same as the K absorption edge energy E_0 of ruthenium oxide. Here, the energy E_0 of the absorption edge means the energy of the first inflection point in the spectrum around the X-ray absorption edge.

10 Then, the pre-edge background was determined by fitting of the data before the edge to the Victoreen formula ($A\lambda^3 - B\lambda^4 + C$ in which λ is a wavelength of the incident X-ray, and A, B and C are constants), and subtracted from the measured values, and then the EXAFS
15 function $\chi(k)$ is extracted by subtracting the smooth background absorption by the isolated atoms estimated by the weighted cubic spline method. The wave number "k" of photoelectrons is defined as $k = 5.123 \times (E - E_0)^{1/2}$ in the unit of nm^{-1} .

20 Finally, the EXAFS function $k^3\chi(k)$, which is weighed by k^3 , is Fourier transformed in the range of k from 27 nm^{-1} to 159 nm^{-1} to obtain the radial distribution function. Here, the Hanning function was used as the window function of the Fourier transform, and the window width was 0.5 nm^{-1} .

25 As ruthenium oxide having a particle size of 10 nm or

more, ruthenium oxide manufactured by NE Chemcat (average particle size: 25.9 nm) was used, and the radial distribution function was obtained in the same manner as in the case of above Catalyst b.

5 The peak intensity ratio $A(b)$ was 0.69, when it was calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the radial distribution function near 0.32 nm.

10 The above-obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 1.8 hours after the start of the reaction, the chlorine
15 formation activity per unit mass of the catalyst C(b) was 6.55×10^{-4} mol/min.g-cat.

2) The second catalyst of this Example was prepared as follows.

20 A commercially available α -alumina powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.1 g), ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.62 g), pure water (3.0 g) and alumina sol (ALUMINA SOL 200 manufactured by Nissan Chemical Industries, Ltd.) (8.53 g) were thoroughly mixed. A dry air was blown
25 onto the mixture at room temperature to dry the mixture

until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain brown noodle-form ruthenium oxide- α -alumina.

The obtained brown noodle-form ruthenium oxide- α -alumina was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain gray noodle-form ruthenium oxide catalyst supported on α -alumina (25.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.5 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass } \%$$

The obtained catalyst was named "Catalyst a".

Then, Catalyst a (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 2.18×10^{-4} mol/min.g-cat.

To measure B(b) of Catalyst b, the following test reaction was carried out:

Catalyst a (0.25 g) was charged in a quartz tube

reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was thoroughly mixed with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g) to dilute Catalyst b, and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360 \pm 1°C, and maintain the internal temperature (hot spot) at 360 \pm 1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 3.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst D(b) was 5.75×10^{-4} mol/min.g-cat.

Then, the peak intensity ratio $B(b)$ of Catalyst b after the reaction was calculated in the same way as in the calculation of the peak intensity ratio $A(b)$ by the EXAFS method. The $B(b)$ ratio was 0.80.

5 Thus, $B(b)/A(b)$ was 1.16.

The ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, $D(b)/C(b)$ was 0.88.

Example 13

10 1) A catalyst of this Example was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (800 g) and an organic binder (16 g) were well mixed. To this mixture, pure water (360 g) and titanium oxide sol (CSB
15 (TiO_2 content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (133 g) were added, mixed and well kneaded.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air
20 at 110°C for 14 hours to obtain white noodle-form titanium oxide. The noodle-form solid was cut to a length of about 5 to 3 mm to obtain white titanium oxide solid.

Then, the solid (450 g) was heated from room temperature to 700°C over 3 hours and calcined at the same
25 temperature for 3 hours to obtain the extruded white

titanium oxide carrier (434 g).

Thereafter, the carrier (50.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 39.6 mass %) (5.78 g) dissolved in pure water (23.5 ml), dried at room temperature for 3 hours and dried at 60°C for 20 minutes, and then at 110°C for 14 hours.

The obtained solid was heated from room temperature to 300°C over 2.0 hours while supplying an air at a flow rate of 1 l/min. and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (52.8 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.65 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.3 \text{ mass \%}$$

The obtained catalyst is named "Catalyst b".

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

The peak intensity ratio A(b) was 0.49, when it was calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the

radial distribution function near 0.32 nm.

The above-obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was
5 carried out in the same manner as that in Example 1. When 1.8 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 6.9×10^{-4} mol/min.g-cat.

2) To measure B(b) of Catalyst b, the following test
10 reaction was carried out:

Catalyst a (0.25 g) was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical
15 α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were
20 supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in
25 the catalyst layer in the range of $320-360 \pm 1^\circ\text{C}$, and

maintain the internal temperature (hot spot) at $360 \pm 1^\circ\text{C}$. Then, the reaction was continued for 50 hours under the above conditions.

Then, the peak intensity ratio $B(b)$ of Catalyst b
5 after the reaction was calculated in the same way as in the calculation of the peak intensity ratio $A(b)$ by the EXAFS method. The $B(b)$ was 0.67.

Thus, $B(b)/A(b)$ was 1.37.

Example 14

10 A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the
15 mixture, pure water (22.6 g) and titanium oxide sol (CSB (TiO_2 content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature while drying.

This mixture was molded by extrusion in the form of
20 noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide- α -alumina.

Then, 36.1 g of this solid from the obtained white noodle-form titanium oxide- α -alumina was heated under air
25 from room temperature to 600°C over 1.7 hours and calcined

at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (35.4 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium
5 oxide- α -alumina carrier.

Then, the carrier (30.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (2.39 g) dissolved in pure water (7.00 g), dried at room
10 temperature overnight and further dried at 60°C for 2 hours.

The obtained solid was heated from room temperature to 350°C over 1.8 hours while supplying an air at a flow rate of 200 ml/l and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst
15 supported on titanium oxide- α -alumina (31.0 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

20
$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass } \%$$

The obtained catalyst was named "Catalyst b".

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

25 The peak intensity ratio A(b) was 0.66, when it was

calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the radial distribution function near 0.32 nm.

5 The above-obtained ruthenium oxide catalyst supported on titanium oxide- α -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the oxygen gas was supplied at a flow
10 rate of 206 ml/min. and the internal temperature (hot spot) was maintained at 301°C. When 2 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst C(b) was 5.15×10^{-4} mol/min.g-cat.

15 To measure the chlorine formation activity after 50 hours reaction D(b), the following test reaction was carried out.

20 Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a
25 reactor in this order from the inlet of the reactor. Then,

hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the internal temperature (hot spot) at 360±1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride was supplied at a flow rate of 190 ml/min. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst D(b) was 4.1×10^{-4} mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, D(b)/C(b) was 0.80.

Example 15

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal)

manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the mixture, pure water (22.5 g) and titanium oxide sol (CSB
5 (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, added and well kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air
10 at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina.

The white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to
15 obtain white noodle-form titanium oxide- α -alumina (54.8 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

Then, the carrier (45.0 g) was impregnated with an
20 aqueous solution of commercially available ruthenium chloride (RuCl₃.nH₂O, ruthenium content: 38.2 mass %) (3.53 g) dissolved in pure water (15.6 g), dried at room temperature overnight and further dried at 60°C for 2 hours.

Then, 21 g of this solid from the obtained one (48.5
25 g) was heated from room temperature to 300°C over 1.5 hours

while supplying an air at a flow rate of 200 ml/l and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide- α -alumina (20.2 g).

5 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2+\alpha\text{-Al}_2\text{O}_3)] \times 100 = 3.8 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+ \text{TiO}_2+\alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.9 \text{ mass \%}$$

10 The obtained catalyst was named "Catalyst b".

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

15 The peak intensity ratio A(b) was 0.49, when it was calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the radial distribution function near 0.32 nm.

20 The above-obtained ruthenium oxide catalyst supported on titanium oxide- α -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the oxygen gas was supplied at a flow rate of 193 ml/min. When 2.2 hours after the start of the
25 reaction, the chlorine formation activity per unit mass of

the catalyst C(b) was 5.5×10^{-4} mol/min.g-cat.

To measure the chlorine formation activity D(b) after 50 hours reaction, the following test reaction was carried out.

5 Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by
10 mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalyst a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the
15 quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst
20 layer in the range of $320-360 \pm 1^\circ\text{C}$, and maintain the internal temperature (hot spot) at $360 \pm 1^\circ\text{C}$. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of
25 its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1 except that Catalyst b was diluted with the commercially available spherical α -alumina carrier having a diameter of 2 mm (20 g) and then charged in the reactor, and the reaction was carried out in the same manner as that in Example 1. When 1.8 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst D(b) was 4.5×10^{-4} mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, D(b)/C(b) was 0.81.

Example 16

A catalyst of this Example was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (510 g), aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (990 g) and an organic binder (15 g) were well mixed. To this mixture, pure water (371 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (197 g) were added, mixed and well kneaded.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 110°C for 14 hours to obtain white noodle-form titanium

oxide- α -alumina. The noodle-form solid was cut to a length of about 3 to 5 mm to obtain white titanium oxide- α -alumina solid.

Then, a sample of 450 g from the obtained solid was
5 heated from room temperature to 600°C over 3 hours and calcined at the same temperature for 3 hours to obtain the extruded white titanium oxide- α -alumina carrier (443 g).

Thereafter, the carrier (50.0 g) was impregnated with an aqueous solution of commercially available ruthenium
10 chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 39.6 mass %) (1.96 g) dissolved in pure water (13.4 ml), kept standing at room temperature for 3 hours and dried at 60°C for 20 minutes, and then at 110°C for 14 hours.

The obtained solid (52.7 g) was heated from room
15 temperature to 300°C over 2.0 hours while supplying an air at a flow rate of 1 l/min. and calcined at the same temperature for 2 hours to obtain an extruded black ruthenium oxide catalyst supported on titanium oxide (50.8 g).

20 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.0 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass \%}$$

25 The obtained catalyst is named "Catalyst b".

The obtained ruthenium oxide catalyst supported on titanium oxide- α -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 299°C. When 2.1 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst C(b) was 3.83×10^{-4} mol/min.g-cat.

To measure the chlorine formation activity D(b) after 50 hours reaction, the following test reaction was carried out.

Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in

the catalyst layer in the range of $320-360\pm 1^{\circ}\text{C}$, and maintain the internal temperature (hot spot) at $360\pm 1^{\circ}\text{C}$. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride was supplied at a flow rate of 190 ml/min. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst D(b) was 3.26×10^{-4} mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, $D(b)/C(b)$ was 0.85.

Example 17

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.7 g) and titanium oxide sol (CSB (TiO_2 content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature.

The mixture was molded by extrusion in the form of

noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide (57.3 g).

5 The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide (55.6 g).

10 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (30.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (3.58 g) dissolved in pure water (10.1 g) and dried at room
15 temperature overnight to obtain the supported ruthenium chloride solid (41.2 g).

Then, 10.3 g of this solid from the supported ruthenium chloride one was dried at 350°C for 2 hours while supplying nitrogen gas at a flow rate of 192 ml/min. to
20 obtain an extruded black catalyst supported on titanium oxide (7.88 g).

The above-obtained catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in
25 the same manner as that in Example 1. When 1.8 hours after

the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 6.15×10^{-4} mol/min.g-cat.

Example 18

1) A catalyst was prepared as follows.

5 To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (50.0 g), pure water (35.1 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (6.6 g) were added and kneaded.

10 The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide (40.2 g). The same operation was repeated. In total, 80.7 g of the white noodle-form titanium oxide was obtained.

15 The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide.

20 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl₃.nH₂O, ruthenium content: 37.3 mass %) (2.55 g) dissolved in pure water (8.65 g), and dried at 60°C for

25

2 hours.

Then, the obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (13.2 g), pure water (120 g) and hydrazine monohydrate (3.21 g).

5 Bubbling was observed as soon as the dried solid was dipped in the solution. After 60 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and
10 filtration were repeated five times. The pH of the first wash liquid was 9.0, and that of the fifth wash liquid was 6.3.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred,
15 followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the black solid (21.0 g).

Then, the black solid was heated under air from room
20 temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the black solid (20.5 g).

After calcination, pure water (500 ml) was added to the black solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation
25 was repeated five times. Thereafter, an aqueous solution

of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded black ruthenium oxide catalyst supported
5 on titanium oxide.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 5.9 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

10
$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2)] \times 100 = 4.5 \text{ mass \%}$$

With Catalyst b, the peak intensity ratio A(b) of the radial distribution function was measured by the EXAFS method in the same manner as that in Example 12.

The peak intensity ratio A(b) was 0.41, when it was
15 calculated by dividing the peak intensity of Catalyst b by the peak intensity of ruthenium oxide having the particle size of 10 nm or more with respect to the peak of the radial distribution function near 0.32 nm.

The above-obtained ruthenium oxide catalyst supported
20 on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 299°C. When 2.7 hours after the start of the reaction, the
25 chlorine formation activity per unit mass of the catalyst

was 8.75×10^{-4} mol/min.g-cat.

2) To measure B(b) of Catalyst b, the following test reaction was carried out:

Catalyst a (0.25 g), which is the same as Catalyst a
5 used in Example 12, was charged in a quartz tube reactor
having an inner diameter of 14 mm without dilution from the
inlet of the reactor. Catalyst b (2.50 g) was diluted by
mixing with the commercially available spherical α -alumina
carrier having a diameter of 2 mm (SSA 995 manufactured by
10 NIKKATO) (20 g), and diluted Catalyst b was charged in the
quartz reactor. The catalysts a and b were charged in a
reactor in this order from the inlet of the reactor. Then,
hydrogen chloride gas and oxygen gas were supplied in the
quartz reactor tube under atmospheric pressure at flow
15 rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26
mol/h), respectively (each converted to a volume at 0°C
under 101 kPa.) The quartz reactor tube was heated in an
electric furnace to keep the temperature in the catalyst
layer in the range of $320-360 \pm 1^\circ\text{C}$, and maintain the
20 internal temperature (hot spot) at $360 \pm 1^\circ\text{C}$. Then, the
reaction was continued for 50 hours under the above
conditions. After that, Catalyst b was recovered, and
recovered Catalyst b was subjected to the measurement of
its chlorine formation activity.

25 That is, recovered Catalyst b (2.5 g) was filled in

the reactor in the same manner as that in Example 1 except that Catalyst b was diluted with the commercially available spherical α -alumina having a diameter of 2 mm (20 g) by mixing them thoroughly and then charged in the reactor, and
5 the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 6.5×10^{-4} mol/min.g-cat.

Then, the peak intensity ratio B(b) of Catalyst b
10 after the reaction was calculated in the same manner as in the calculation of the peak intensity ratio A(b) by the EXAFS method. The B(b) ratio was 0.62

Thus, B(b)/A(b) was 1.51.

The ratio of the catalytic activity after the 50 hours
15 reaction to the initial catalytic activity, D(b)/C(b) was 0.74.

Example 19

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal)
20 manufactured by Sakai Chemical Industry Co., Ltd.) (25.0 g) and aluminum oxide powder (AL-31 manufactured by Sumitomo Chemical Co., Ltd.) (25.0 g) were thoroughly mixed. To the mixture, pure water (18.9 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical
25 Industry Co., Ltd.) (6.6 g) were added and kneaded.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 2 hours to obtain white noodle-form titanium oxide- α -alumina (47.1 g).

5 24.5 Grams of the solid from the white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina.

10 After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (0.805 g) dissolved in pure water (5.82 g) and dried at 60°C for 2 hours.

Then, the obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (4.2 g), pure water (120 g) and hydrazine monohydrate (1.03 g). Bubbling was observed as soon as the dried solid was dipped in the solution. After 60 minutes, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and

filtration were repeated five times. The pH of the first wash liquid was 9.0, and that of the fifth wash liquid was 6.5.

To the filtrated solid, a 0.5 mol/l aqueous solution
5 of potassium chloride (50 g) was added, and stirred,
followed by recovering of the solid by filtration. The
same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to
obtain the black solid.

10 Then, the black solid was heated under air from room
temperature to 350°C over 1 hour and calcined at the same
temperature for 3 hours to obtain the black solid.

After calcination, pure water (500 ml) was added to
the black solid and the mixture was stirred, followed by
15 recovering of the solid by filtration. The same operation
was repeated five times. Thereafter, an aqueous solution
of silver nitrate was dropwise added to the wash liquid to
confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to
20 obtain an extruded black ruthenium oxide catalyst supported
on titanium oxide- α -alumina (20.2 g).

The calculated content of ruthenium oxide was as
follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass \%}$$

25 The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass \%}$$

The above-obtained ruthenium oxide catalyst supported on titanium oxide- α -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the
5 reaction was carried out in the same manner as that in Example 1.

To measure the chlorine formation activity D(b) after 50 hours reaction, the following test reaction was carried out.

10 Catalyst a (0.25 g), which is the same as Catalyst a used in Example 12, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by
15 mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96
20 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the internal temperature (hot spot) at 360±1°C.
25 Then, the reaction was continued for 50 hours under the

above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1.

Example 20

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.7 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide (57.3 g).

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide (55.6 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium

oxide carrier.

Then, the carrier (30.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (3.58 g) dissolved in pure water (10.1 g) and dried at room temperature overnight to obtain the supported ruthenium chloride solid (41.2 g).

Then, 10.3 g of this solid from the supported ruthenium chloride one was dried at 150°C for 2 hours while supplying nitrogen gas at a flow rate of 192 ml/min. to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (8.14 g).

The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.56 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.17 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 301°C . When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was $6.05 \times 10^{-4} \text{ mol/min.g-cat.}$

Example 21

10.3 Grams of solid from the undried supported ruthenium chloride on the titanium oxide carrier, which is the solid prepared in Example 20, was dried at 60°C for 2
5 hours while supplying nitrogen gas at a flow rate of 200 ml/min. to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (8.40 g).

The calculated content of ruthenium chloride was as follows:

10
$$[\text{RuCl}_2/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 8.56 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 4.17 \text{ mass } \%$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the
15 reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 5.85×10^{-4} mol/min.g-cat.

20 Example 22

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.7 g) and titanium oxide sol (CSB
25 (TiO₂ content: 38 mass %) manufactured by Sakai Chemical

Industry Co., Ltd.) (7.9 g) were added and well kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air
5 at 60°C for 4 hours to obtain white noodle-form titanium oxide (59.5 g).

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-
10 form titanium oxide (57.8 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (10.0 g) was impregnated with an
15 aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (1.19 g) dissolved in pure water (4.93 g), dried at room temperature overnight and further dried under air at 150°C for 2 hours to obtain an extruded black ruthenium chloride
20 catalyst supported on titanium oxide (10.9 g).

The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.56 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

25
$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.17 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 7.0×10^{-4} mol/min.g-cat.

Example 23

A catalyst was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (60.0 g), pure water (44.8 g) and titanium oxide sol (CSB (TiO_2 content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added and well kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide (58.0 g).

The obtained titanium oxide solid was heated under air from room temperature to 700°C over 1.9 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide (56.5 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium

oxide carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (2.39 g) dissolved in pure water (10.4 g), dried at room temperature overnight and further dried under air at 100°C for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (14.3 g).

The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.56 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.17 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide was filled in the reactor in the same manner as that in Example 1 except that the ruthenium chloride catalyst supported on titanium oxide (1 g) was diluted with the commercially available spherical α -alumina carrier having a particle size of 2 mm (20 g) by mixing, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was $11.8 \times 10^{-4} \text{ mol/min.g-cat.}$

Example 24

1) The solid from the undried supported ruthenium

chloride on the titanium oxide carrier, which is prepared in Example 23, was dried under air at 60°C for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (8.0 g).

5 The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 8.56 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 4.17 \text{ mass } \%$$

10 This catalyst was named "Catalyst b".

The above-obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in
15 Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst E(b) was 6.45×10^{-4} mol/min.g-cat.

The same ruthenium chloride catalyst supported on titanium oxide (1.0 g) was filled in the reactor in the
20 same manner as that in Example 1 except that the ruthenium chloride catalyst supported on titanium oxide (1 g) was diluted with the commercially available spherical α -alumina carrier having a particle size of 2 mm (20 g) by mixing, and the reaction was carried out in the same manner as that
25 in Example 1. When 2.0 hours after the start of the

reaction, the chlorine formation activity per unit mass of the catalyst was 11.2×10^{-4} mol/min.g-cat.

2) The second catalyst of this Example was prepared as follows.

5 A commercially available α -alumina (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.1 g), ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.62 g), pure water (3.0 g) and alumina sol (ALUMINA SOL 200 manufactured by Nissan Chemical Industries, Ltd.) (8.53 g) were thoroughly mixed. A dry air was blown
10 onto the mixture at room temperature to dry the mixture until an adequate viscosity was reached.

 This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air
15 at 60°C for 4 hours to obtain brown noodle-form ruthenium oxide- α -alumina.

 The obtained noodle-form solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain gray noodle-form
20 ruthenium oxide catalyst supported on α -alumina (25.8 g).

 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.5 \text{ mass \%}$$

 The calculated content of ruthenium was as follows:

25
$$[\text{Ru} / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.9 \text{ mass \%}$$

The obtained catalyst was named "Catalyst a".

3) To measure the chlorine formation activity after 50 hours reaction F(b), the following test reaction was carried out.

5 Catalyst a (0.25 g) was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995
10 manufactured by NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalysts a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric
15 pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360 \pm 1°C, and
20 maintain the hot spot of Catalyst b at 360 \pm 1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

25 That is, recovered Catalyst b (2.4 g) was filled in

the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 1.8 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst F(b) was 7.05×10^{-4} mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, F(b)/E(b) was 1.09.

Example 25

A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (48.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (12.0 g) were thoroughly mixed. To the mixture, pure water (39.5 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added and well kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina (57.0 g).

The obtained titanium oxide- α -alumina solid was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to obtain

white noodle-form titanium oxide- α -alumina (55.6 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

5 Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (1.99 g) dissolved in pure water (10.1 g), dried at room temperature overnight and further dried under air at 60°C
10 for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (21.9 g).

The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 7.24 \text{ mass \%}$$

15 The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 3.52 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on the titanium oxide- α -alumina carrier (2.5 g) was filled in the reactor in the same manner as that in
20 Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was 301°C. When 2.5 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was $6.95 \times 10^{-4} \text{ mol/min.g-cat.}$

25 Example 26

1) A catalyst was prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and aluminum oxide powder (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed. To the mixture, pure water (22.5 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.9 g) were added, mixed and well kneaded at room temperature.

The mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina (56.3 g).

The obtained titanium oxide- α -alumina solid was heated under air from room temperature to 600°C over 1.7 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (55.4 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

Then, the carrier (20.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride (RuCl₃.nH₂O, ruthenium content: 38.2 mass %) (1.59 g) dissolved in pure water (6.40 g), dried at room temperature overnight and further dried under air at 60°C

for 2 hours to obtain an extruded black ruthenium chloride catalyst supported on titanium oxide (21.5 g).

The calculated content of ruthenium chloride was as follows:

$$5 \quad [\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 5.87 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2 + \alpha\text{-alumina})] \times 100 = 2.86 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on titanium oxide- α -alumina (2.5 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 301°C. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst E(b) was 4.98×10^{-4} mol/min.g-cat.

2) To measure the chlorine formation activity after 50 hours reaction F(b), the following test reaction was carried out.

Catalyst a (0.25 g), which was a ruthenium chloride catalyst supported on α -alumina prepared in the same manner as that in Example 24, was charged in a quartz tube reactor having an inner diameter of 14 mm without dilution from the inlet of the reactor. Catalyst b (2.50 g) was diluted by mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by

NIKKATO) (20 g), and diluted Catalyst b was charged in the quartz reactor. The catalysts a and b were charged in a reactor in this order from the inlet of the reactor. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. (0.51 mol/h) and 96 ml/min. (0.26 mol/h), respectively (each converted to a volume at 0°C under 101 kPa.) The quartz reactor tube was heated in an electric furnace to keep the temperature in the catalyst layer in the range of 320-360±1°C, and maintain the hot spot of Catalyst b at 360±1°C. Then, the reaction was continued for 50 hours under the above conditions. After that, Catalyst b was recovered, and recovered Catalyst b was subjected to the measurement of its chlorine formation activity.

That is, recovered Catalyst b (2.3 g) was filled in the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst F(b) was 4.96×10^{-4} mol/min.g-cat.

Thus, the ratio of the catalytic activity after the 50 hours reaction to the initial catalytic activity, F(b)/E(b) was 1.0.

Comparative Example 1

A catalyst was prepared as follows.

Commercially available ruthenium chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 35.5 mass %) (0.70 g) was dissolved in pure water (4.0 g). After the aqueous solution was sufficiently stirred, it was dropwise added to silica (CARIACT G-10 manufactured by Fuji Silysia Chemical Co.) (5.0 g), the particle sizes of which had been adjusted in the range between 0.85 and 1.4 mm and which had been dried under air at 500°C for 1 hour to support ruthenium chloride on the silica particles. The supported one was heated from room temperature to 100°C over 30 minutes while supplying nitrogen gas at a flow rate of 100 ml/min. and dried at the same temperature for 2 hours, followed by spontaneous cooling to room temperature to obtain a black solid.

The obtained solid was heated from room temperature to 250°C over 1.5 hours while supplying the air at a rate of 100 ml/min. and dried at the same temperature for 3 hours, followed by spontaneous cooling to room temperature to obtain a black ruthenium chloride catalyst supported on silica.

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + \text{SiO}_2)] \times 100 = 4.5 \text{ mass \%}$$

The above-obtained ruthenium chloride catalyst supported on silica (2.5 g) without dilution was filled in

the reactor in the same manner as that in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride and oxygen were supplied at flow rates of 202 ml/min. and 213 ml/min., respectively. When 1.7 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 0.49×10^{-4} mol/min.g-cat.

Comparative Example 2

A catalyst was prepared as follows.

Spherical titanium oxide (CS-300 manufactured by Sakai Chemical Industry Co., Ltd.) was ground with a mortar to obtain titanium oxide powder. The titanium oxide powder (8.0 g) and ruthenium dioxide powder (0.53 g) were mixed in a mortar while grinding, followed by molding in the form of particles having sizes of 0.85 to 1.4 mm to obtain a ruthenium oxide-titanium oxide mixed catalyst. The calculated content of ruthenium oxide was 6.2 mass %, and that of ruthenium was 4.7 mass %.

The above-obtained ruthenium oxide-titanium oxide mixed catalyst (2.5 g) was diluted by mixing with a titanium oxide carrier having adjusted particle sizes of 0.85 to 1.4 mm (5 g), and the diluted catalyst was charged in a quartz tube reactor having an inner diameter of 12 mm. Then, the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride and oxygen

were supplied at flow rates of 199 ml/min. and 194 ml/min., respectively, and the internal temperature (hot spot) was maintained at 299°C. When 2.3 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 0.83×10^{-4} mol/min.g-cat.

Comparative Example 3

A catalyst was prepared as follows.

Commercially available tetraethyl orthosilicate (41.7 g) was dissolved in ethanol (186 ml). To the solution, titanium tetraisopropoxide (56.8 g) was added, and the mixture was stirred at room temperature for 30 minutes. Then, to this solution, an aqueous solution was dropwise added, which was prepared by well mixing ethanol (93 ml) with a 0.01 mol/l aqueous solution of acetic acid that had been prepared by dissolving acetic acid (0.14 g) in pure water (233 ml). White precipitates formed as the aqueous solution was dropwise added. After the dropwise addition, the mixture was stirred at room temperature for 30 minutes. Thereafter, the mixture was heated to reflux on an oil bath maintained at 102°C for 1 hour while stirring, during which the temperature of the liquid was 80°C. Then, the liquid was spontaneously cooled, filtrated with a glass filter, washed with water (500 ml) and again filtrated. This operation was repeated twice. Thereafter, the product was dried under air at 60°C for 4 hours, heated from room

temperature to 550°C over 1 hour, and calcined at the same temperature for 3 hours to obtain a white solid (27.4 g). The white solid was ground to obtain titania-silica powder.

The obtained titania-silica powder (8.0 g) was
5 impregnated with an aqueous solution of commercially available ruthenium chloride hydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, ruthenium content: 35.5 mass %) (1.13 g) in pure water (8.2 g), and dried at 60°C for 1 hour to support ruthenium chloride on the titania-silica powder. Then, the titania-silica powder
10 supporting ruthenium chloride was reduced by heating it from room temperature to 300°C over 1.5 hours and then at the same temperature for 1 hour while supplying the mixture of hydrogen gas and nitrogen gas at flow rates of 50 ml/min. and 100 ml/min., respectively, followed by spontaneously
15 cooling to room temperature to obtain a grayish brown metal ruthenium supported on the titania-silica powder (8.4 g).

The obtained metal ruthenium supported on the titania-silica powder (8.4 g) was heated from room temperature to 600°C over 3 hours and 20 minutes and calcined at the same
20 temperature for 3 hours while supplying an air at a flow rate of 100 ml/min. to obtain the gray powder (8.5 g). The gray powder was molded in the form of particles having sizes of 0.85 to 1.4 mm to obtain a ruthenium oxide catalyst supported on titania-silica.

25 The calculated content of ruthenium oxide was as

follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2+\text{SiO}_2)] \times 100 = 6.2 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2+\text{SiO}_2)] \times 100 = 4.7 \text{ mass \%}$$

5 The obtained ruthenium oxide catalyst supported on
titania-silica (2.5 g) without dilution was charged in the
quartz reactor tube, and the reaction was carried out in
the same manner as that in Example 1 except that hydrogen
chloride gas and oxygen gas were supplied at flow rates of
10 180 ml/min. and 180 ml/min., respectively.

When 1.8 hours after the start of the reaction, the
chlorine formation activity per unit mass of the catalyst
was 0.46×10^{-4} mol/min.g-cat.

Comparative Example 4

15 A catalyst was prepared as follows.

A spherical titanium oxide carrier having a diameter
of 1 to 2 mm (CS-300S-12 manufactured by Sakai Chemical
Industry Co., Ltd.) (10.1 g) was impregnated with an
aqueous solution of commercially available ruthenium
20 chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3
mass %) (1.34 g) in pure water (3.7 g), and dried under air
at 60°C for 4 hours to obtain a dark brown solid. This
dark brown solid was reduced by heating it from room
temperature to 250°C over 2 hours and then at the same
25 temperature for 8 hours while supplying the mixture of

hydrogen gas and nitrogen gas at flow rates of 20 ml/min. and 200 ml/min., respectively to obtain the black solid (10.3 g).

Then, the obtained solid was heated under air from
5 room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain a black ruthenium oxide catalyst supported on titanium oxide (10.6 g).

The calculated content of ruthenium oxide was as follows:

10
$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 6.1 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 4.7 \text{ mass } \%$$

The obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) was diluted with the commercially
15 available spherical titanium oxide having a diameter of 1 to 2 mm (CS-300S-12 manufactured by Sakai Chemical Industry Co., Ltd.) (5 g) by mixing them thoroughly and then charged in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in
20 Example 1 except that hydrogen chloride gas and oxygen gas were supplied at flow rates of 187 ml/min. and 199 ml/min., respectively.

When 2 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst
25 was 2.89×10^{-4} mol/min.g-cat.

Comparative Example 5

A catalyst was prepared as follows.

5 A spherical metal ruthenium catalyst supported on titanium oxide having a diameter of 1 to 2 mm (5 mass % supported on anatase titanium oxide) (manufactured by N.E. Chemcat) was impregnated with a 0.5 mol/l aqueous solution of potassium chloride to an extent that the solution oozed out on the surface of the catalyst, and dried under air at 60°C for 1 hour. The same operation was repeated twice.

10 The impregnated amount of the aqueous solution of potassium chloride was 3.31 g in the first operation and 3.24 g in the second operation. Thus, the total impregnated amount of the aqueous solution of potassium chloride was 6.55 g. The calculated molar ratio of potassium chloride to
15 ruthenium was 0.66.

The dried catalyst was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours. Then, the calcined catalyst was washed with pure water (500 ml) for 30 minutes, followed by
20 filtration. The washing and filtration were repeated five time. An aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained. After washing, the solid was dried at 60°C for 4 hours to obtain black spherical ruthenium oxide
25 supported on titanium oxide (9.9 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 6.6 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

5
$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 5.0 \text{ mass \%}$$

The obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) was diluted with the commercially available spherical titanium oxide having a diameter of 1 to 2 mm (CS-300S-12 manufactured by Sakai Chemical Industry Co., Ltd.) (5 g) by mixing them thoroughly and then charged
10 in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride gas and oxygen gas were supplied at flow rates of 187 ml/min. and 199 ml/min.,
15 respectively.

When 2 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 4.03×10^{-4} mol/min.g-cat.

Comparative Example 6

20 1) The first catalyst of this Comparative Example was prepared as follows.

To titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (50.0 g), pure water (33.6 g) and titanium oxide sol (CSB
25 (TiO_2 content: 38 mass %) manufactured by Sakai Chemical

Industry Co., Ltd.) (6.59 g) were added and kneaded. A dry air was blown onto the kneaded mixture at room temperature to dry the mixture until an adequate viscosity was reached. The mixture was molded by extrusion in the form of noodles
5 having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours.

Separately, to titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (20.0 g), pure water (13.3 g) and titanium oxide sol
10 (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (2.65 g) were added and kneaded. A dry air was blown onto the kneaded mixture at room temperature to dry the mixture until an adequate viscosity was reached. The mixture was molded by extrusion
15 in the form of noodles having a diameter of 1.5 mm ϕ , and dried under air at 60°C for 4 hours.

The two portions of the dried noodle-form solids were mixed and heated under air from room temperature to 500°C over 1.4 hours and calcined at the same temperature for 3
20 hours to obtain white noodle-form titanium oxide (64.8 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide carrier.

Then, the carrier (62.0 g) was impregnated with an
25 aqueous solution of commercially available ruthenium

chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (5.04 g) dissolved in pure water (34.1 g), and dried at 60°C for 2 hours.

The obtained solid was dipped in a solution containing
5 2N aqueous solution of potassium hydroxide (26.1 g), pure water (372 g) and hydrazine monohydrate (6.33 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 1 hour, the supernatant was removed by filtration. Then, pure water (500 ml) was added to the
10 recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.0, and that of the fifth wash liquid was 7.2.

To the filtrated solid, a 0.5 mol/l aqueous solution
15 of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

20 Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.

After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed
25 by recovering of the solid by filtration. The same

operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to
5 obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide (62.6 g).

A packing density of the obtained catalyst was 0.77.

The calculated content of ruthenium oxide was as follows:

10
$$[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 3.8 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 2.9 \text{ mass } \%$$

The obtained catalyst is named "Catalyst c".

2) The second catalyst of this Comparative Example was
15 prepared as follows.

Titanium oxide powder (STR-60R (100 % rutile crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (30.0 g) and aluminum oxide powder (AL-31-03 manufactured by Sumitomo Chemical Co., Ltd.) (30.0 g) were thoroughly mixed.
20 To the mixture, pure water (19.6 g) and titanium oxide sol (CSB (TiO₂ content: 38 mass %) manufactured by Sakai Chemical Industry Co., Ltd.) (7.91 g) were added and kneaded.

This mixture was molded by extrusion in the form of
25 noodles having a diameter of 1.5 mmφ, and dried under air

at 60°C for 4 hours to obtain white noodle-form titanium oxide- α -alumina.

The white noodle-form titanium oxide- α -alumina was heated under air from room temperature to 500°C over 1.4
5 hours and calcined at the same temperature for 3 hours to obtain white noodle-form titanium oxide- α -alumina (55.7 g).

After calcination, the noodle-form solid was cut to a length of about 5 mm to obtain an extruded white titanium oxide- α -alumina carrier.

10 Then, the carrier (45.0 g) was impregnated with an aqueous solution of commercially available ruthenium chloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 37.3 mass %) (1.83 g) dissolved in pure water (14.0 g) and dried at 60°C for 2 hours.

15 Then, the obtained solid was dipped in a solution containing 2N aqueous solution of potassium hydroxide (9.49 g), pure water (270 g) and hydrazine monohydrate (2.30 g). Bubbling was observed as soon as the calcined solid was dipped in the solution. After 60 minutes, the supernatant
20 was removed by filtration. Then, pure water (500 ml) was added to the recovered solid and the solid was washed for 30 minutes, followed by filtration. The washing and filtration were repeated five times. The pH of the first wash liquid was 9.2, and that of the fifth wash liquid was
25 7.2.

To the filtrated solid, a 0.5 mol/l aqueous solution of potassium chloride (50 g) was added, and stirred, followed by recovering of the solid by filtration. The same operation was repeated three times.

5 The obtained solid was dried at 60°C for 4 hours to obtain the gray solid.

Then, the gray solid was heated under air from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain the bluish gray solid.

10 After calcination, pure water (500 ml) was added to the bluish gray solid and the mixture was stirred, followed by recovering of the solid by filtration. The same operation was repeated five times. Thereafter, an aqueous solution of silver nitrate was dropwise added to the wash
15 liquid to confirm that no potassium chloride remained.

Thereafter, the solid was dried at 60°C for 4 hours to obtain an extruded bluish gray ruthenium oxide catalyst supported on titanium oxide- α -alumina (45.4 g).

The packing density of this catalyst was 0.97.

20 The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.0 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.5 \text{ mass \%}$$

25 This catalyst was named "Catalyst b".

3) In a glass test reactor tube having an inner diameter of 15 mm ϕ , in which a thermocouple-protective tube having an outer diameter of 6 mm was inserted, Catalyst a, which is the same as Catalyst a of Example 1, and above-
5 prepared Catalysts b and c were charged in a volume ratio of 2:13:5 (a:b:c) from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of α -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts
10 a, b and c were as follows:

Catalyst a: 1.73 ml (2.27 g)

Catalyst b: 11.25 ml (10.88 g)

Catalyst c: 4.32 ml (3.33 g)

The total volume of charged catalysts was 17.3 ml.

15 The upper zone of the catalyst layer was formed by Catalyst a and Catalyst b, while the lower zone of the catalyst layer was formed by Catalyst c, and each zone was heated with a respective electric furnace.

From the start of the reaction to 54 hours, hydrogen
20 chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 127 ml/min. and 66 ml/min. respectively (each converted to a volume at 0°C under 101 kPa.), and from 54 hours to 80 hours from the start of the reaction,
25 hydrogen chloride gas and oxygen gas were supplied and

flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 130 ml/min. and 66 ml/min. respectively (each converted to a volume at 0°C under 101 kPa.) During the reaction, the conversion of hydrogen chloride was maintained at higher than 70 %. After 80 hours, the internal temperature (hot spot) of the upper zone in the test reactor tube was 341°C, while that of the lower zone was 302°C. At this time, the gas from the outlet of the test reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively. The conversion of hydrogen chloride was 91.0 %.

4) Thereafter, the activity of Catalyst c was measured as follows:

The activity of Catalyst c was represented by $M(c)$.

Catalyst c was isolated from the mixture of Catalyst c and the α -alumina carrier used in the step 3). Using this Catalyst c, the activity $M(c)$ was measured in the same manner as that for the measurement of $M(c)$ in Example 1 except that 2.5 g of Catalyst c was diluted by mixing with the commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10 g), diluted Catalyst c was charged in a quartz reactor

tube having an inner diameter of 12 mm, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 192 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.), and the internal temperature (hot spot) was maintained at 300°C. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was 7.1×10^{-4} mol/min.g-cat.

5) In a glass test reactor tube having an inner diameter of 14 mm, in which a thermocouple-protective tube having an outer diameter of 5 mm was inserted, Catalyst a, which is the same as Catalyst a of Example 1, and above-prepared Catalysts b and c were charged in a volume ratio of 2:13:5 (a:b:c) from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of α -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Catalysts a, b and c were as follows:

Catalyst a: 1.73 ml (2.27 g)

Catalyst b: 11.25 ml (10.88 g)

Catalyst c: 4.32 ml (3.33 g)

The total volume of charged catalysts was 17.3 ml.

The upper zone of the catalyst layer was formed by Catalyst a and Catalyst b, while the lower zone of the catalyst layer was formed by Catalyst c, and each zone was

heated with a respective electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper zone to the lower zone at flow rates of 130 ml/min. and 64 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 502 hours under the same conditions while maintaining the conversion of hydrogen chloride at higher than 70 %. After 502 hours, the internal temperature (hot spot) of the upper zone in the test reactor tube was 352°C, while that of the lower zone was 302°C. At this time, the gas from the outlet of the test reactor tube was sampled by passing it through an aqueous 30 mass % potassium iodide solution, and the amount of chlorine formed and the amount of unreacted hydrogen chloride were determined by iodometric titration and neutralization titration, respectively. The conversion of hydrogen chloride was 83.3 %.

6) After the step 5), Catalyst c was isolated from the mixture of Catalyst c and the α -alumina carrier used in the step 5), and the activity of Catalyst c N(c) was measured in the same manner as that for the measurement of N(c) in Example 1 except that Catalyst c was diluted with a commercially available spherical α -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10g) by mixing them thoroughly, and diluted Catalyst c was

filled in a quartz reactor tube having an inner diameter of 12 mm.

The chlorine formation activity $N(c)$ was 5.6×10^{-4} mol/min.g-cat.

5 Thus, $N(c)/M(c)$ was 0.79.

Comparative example 7

A catalyst of this Comparative Example was prepared as follows.

10 A spherical titanium oxide carrier (CS-300S (anatase crystal) manufactured by Sakai Chemical Industry Co., Ltd.) was ground to adjust its particle size in the range between 0.85 and 1.4 mm, and then calcined under air at 500°C for 1 hour. Then, the ground titanium oxide carrier (5.0 g) was impregnated with an aqueous solution of commercially
15 available ruthenium chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) (1.41 g) in pure water (3.2 g), and dried by heating it from room temperature to 100°C over 30 minutes and at the same temperature for 2 hours while supplying nitrogen gas at a flow rate of 100 ml/min. Furthermore, the impregnated
20 carrier was heated from 100°C to 250°C over 50 minutes and then at the same temperature for 3 hours to obtain a black ruthenium chloride catalyst supported on titanium oxide (10.5 g).

25 The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 9.3 \text{ mass } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuCl}_2+\text{TiO}_2)] \times 100 = 4.5 \text{ mass } \%$$

The obtained ruthenium chloride catalyst supported on
5 titanium oxide (2.5 g) without dilution was charged in the
reactor in the same manner as in Example 1, and the
reaction was carried out in the same manner as that in
Example 1 except that hydrogen chloride gas and oxygen gas
were supplied at flow rates of 190 ml/min. and 200 ml/min.,
10 respectively.

When 1.7 hours after the start of the reaction, the
chlorine formation activity per unit mass of the catalyst
was 2.97×10^{-4} mol/min.g-cat.

Comparative Example 8

15 A catalyst of this Comparative Example was prepared as
follows.

A spherical titanium oxide carrier (CS-300S (anatase
crystal) manufactured by Sakai Chemical Industry Co., Ltd.)
was ground to adjust its particle size in the range between
20 0.85 and 1.4 mm, and then calcined under air at 500°C for 1
hour. Then, the ground titanium oxide carrier (5.0 g) was
impregnated with an aqueous solution of commercially
available ruthenium chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) (0.70 g)
in pure water (1.4 g), and dried by heating it from room
25 temperature to 100°C over 30 minutes and at the same

temperature for 2 hours while supplying nitrogen gas at a flow rate of 100 ml/min. Furthermore, the impregnated carrier was once cooled to room temperature and heated from room temperature to 350°C over 2 hours and then at the same temperature for 3 hours while supplying an air at a flow rate of 100 ml/min. to obtain a black ruthenium oxide catalyst supported on titanium oxide (5.2 g).

The calculated content of ruthenium oxide was as follows:

10 $[\text{RuO}_2/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 6.2 \text{ mass } \%$

The calculated content of ruthenium was as follows:

$[\text{Ru}/(\text{RuO}_2+\text{TiO}_2)] \times 100 = 4.7 \text{ mass } \%$

The obtained ruthenium oxide catalyst supported on titanium oxide (2.5 g) without dilution was charged in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that hydrogen chloride gas and oxygen gas were supplied at flow rates of 200 ml/min. and 200 ml/min., respectively.

20 When 1.8 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was $2.37 \times 10^{-4} \text{ mol/min.g-cat.}$

Comparative Example 9

A catalyst of this Comparative Example was prepared as follows.

A spherical titanium oxide carrier having a diameter of 1 to 2 mm (CS-300S-12 (anatase crystal) manufactured by Sakai Chemical Industry Co., Ltd.) (20.0 g) was impregnated with an aqueous solution of commercially available

5 ruthenium chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, ruthenium content: 38.2 mass %) (2.38 g) in pure water (7.0 g), and dried at room temperature overnight to obtain the carrier supporting ruthenium chloride (24.7 g). The carrier supporting ruthenium chloride was dried at 60°C for 2 hours.

10 Furthermore, it was dried by heating it under a nitrogen flow (192 ml/min.) from room temperature to 150°C and then at the same temperature for 2 hours to obtain a black ruthenium chloride catalyst supported on titanium oxide (21.3 g).

15 The calculated content of ruthenium chloride was as follows:

$$[\text{RuCl}_2 / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 8.5 \text{ mass \%}$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuCl}_2 + \text{TiO}_2)] \times 100 = 4.2 \text{ mass \%}$$

20 The obtained ruthenium chloride catalyst supported on titanium oxide (2.5 g) was charged in the reactor in the same manner as in Example 1, and the reaction was carried out in the same manner as that in Example 1 except that the internal temperature (hot spot) was maintained at 301°C.

25 When 1.8 hours after the start of the reaction, the

chlorine formation activity per unit mass of the catalyst
was 2.75×10^{-4} mol/min.g-cat.

CLAIMS

1. A supported ruthenium oxide catalyst selected from the group consisting of:

(1) a supported ruthenium oxide catalyst comprising
5 titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

(2) a supported ruthenium oxide catalyst having a
carbon monoxide adsorption amount of at least 87.5 ml per
10 one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60
minutes with flowing a hydrogen gas at a flow rate of 50
ml/min. under atmospheric pressure, and

15 conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,

20 calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of
25 hydrazine and an alkaline compound,

and

oxidizing said hydrazine-treated one.

2. The catalyst according to claim 1, which is said catalyst (2) prepared by the method for the preparation of
5 the catalyst (3) in claim 1.

3. The catalyst according to claim 1, which is said catalyst (2) or (3), wherein said carrier is titanium oxide containing the rutile crystal form.

4. A process for producing a supported ruthenium oxide
10 catalyst or a supported ruthenium chloride catalyst selected from the group consisting of the following processes (1) to (6):

(1) a process comprising the steps of:

supporting a ruthenium compound on a carrier
15 consisting of titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere,
20 an inert gas atmosphere and a reducing gas atmosphere;

(2) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group
25 consisting of an oxidizing gas atmosphere, an inert gas

atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,
and

5 oxidizing said hydrazine-treated one
wherein said supported ruthenium oxide catalyst has a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

10 reducing 0.1 g of said catalyst at 220°C for 60 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse;

15 (3) a process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas
20 atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,
and

oxidizing said hydrazine-treated one;

25 (4) a process comprising the steps of:

supporting a ruthenium compound on a carrier,
and

calcining said supported one in an atmosphere selected
from the group consisting of an oxidizing gas atmosphere,
5 an inert gas atmosphere and a reducing gas atmosphere,
wherein, when the peak intensity ratio of the produced
catalyst and that of the catalyst after a 50 hours reaction
test, which are measured by an extended X-ray absorption
fine structure analysis (EXAFS) method, are A(b) and B(b)
10 respectively, the peak intensity ratios A(b) and B(b)
satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that $A(b) \leq 0.8$,

wherein A(b) is a peak intensity ratio of as-produced
15 Catalyst b measured by the EXAFS method, and B(b) is a peak
intensity ratio of Catalyst b measured by the EXAFS method
after the 50 hours reaction test;
in which

the 50 hours reaction test is carried out by filling
20 supported ruthenium oxide Catalysts a and b in a reactor in
this order from the inlet of the reactor in a weight ratio
of 1:10 (Catalyst a to Catalyst b), and supplying, under
atmospheric pressure, a hydrogen chloride gas at a flow
rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an
25 oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr.

to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat.,

5 which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process,

10 and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst is evaluated by the peak around 0.32 nm in a radial

15 distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity
20 of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a process comprising the following steps but not a treating step with hydrazine:

25 supporting a ruthenium compound on a titanium oxide

carrier containing the rutile crystal form,
and

calcining said supported one at a temperature of 200°C
to 600°C in an atmosphere selected from the group
5 consisting of an oxidizing gas atmosphere, an inert gas
atmosphere and a reducing gas atmosphere;
and

(6) a process comprising the following steps but
neither a calcining step nor a treating step with
10 hydrazine:

supporting a ruthenium halide on a titanium oxide
carrier containing the rutile crystal form,
and

drying said supported one in an atmosphere selected
15 from the group consisting of an oxidizing gas atmosphere,
an inert gas atmosphere and a reducing gas atmosphere at a
temperature of 20°C to less than 200°C.

5. The process according to claim 4, which is the
process (2), (3) or (4), wherein said carrier is titanium
20 oxide containing the rutile crystal form.

6. The process according to claim 4, which is the
process (5), comprising the following steps but not a
treating step with hydrazine:

supporting a ruthenium compound on a carrier,
25 and

10

provided that $C(b) \geq 3.0 \times 10^{-4}$ mol/min·g-cat

15

20

25

the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process, and in which

10 Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical α -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are
15 supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot)
20 at $300 \pm 1^{\circ}\text{C}$, after 2.0 ± 1.0 hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an
25 iodine titration method and a neutralization titration

method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst

5 (mol/min.g-cat.) =

Amount of chlorine gas from reactor exit (mol/min.)/
catalyst weight (g).

7. The process according to claim 4, which is the process (6), comprising the following steps but neither a
10 calcining step nor a treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form,
and

drying said supported one in an atmosphere selected
15 from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C,
wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst
20 after 50 hours reaction test, which are measured by a catalytic activity test which is defined below, are respectively E(b) and F(b), and which satisfy the following equation (3);

$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$

25 provided that $E(b) \geq 3.0 \times 10^{-4}$ mol/min.g-cat.,

in which

50 Hours reaction test: Supported ruthenium oxide Catalysts a and b are filled in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and a hydrogen chloride gas is supplied under atmospheric pressure at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, in which Catalyst a is a supported ruthenium oxide catalyst having a chlorine formation activity per unit mass of the catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process, and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical α -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min.

respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot) at 300±1°C, after 2.0±1.0 hours from the start of the

5 reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration
10 method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst
(mol/min.g-cat.) =

15 Amount of chlorine gas from reactor exit (mol/min.)/
catalyst weight (g).

8. A process for producing chlorine by oxidizing hydrogen chloride with oxygen, which uses at least one catalyst selected from the group consisting of the

20 following catalysts (1) to (6):

(1) a supported ruthenium oxide catalyst comprising titanium oxide which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C, as a carrier;

25 (2) a supported ruthenium oxide catalyst having a

carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst, which is measured by the following steps of:

reducing 0.1 g of said catalyst at 220°C for 60
5 minutes with flowing a hydrogen gas at a flow rate of 50 ml/min. under atmospheric pressure, and

conducting a metal surface area measuring method according to a carbon monoxide pulse;

(3) a supported ruthenium oxide catalyst obtained by a
10 preparation process comprising the steps of:

supporting a ruthenium compound on a carrier,

calcining said supported one at a temperature of at least 200°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas
15 atmosphere and a reducing gas atmosphere,

treating said calcined one with a mixed solution of hydrazine and an alkaline compound,
and

oxidizing said hydrazine-treated one;

(4) a supported ruthenium oxide catalyst produced by a
20 process comprising the steps of:

supporting a ruthenium compound on a carrier,
and

calcining said supported one in an atmosphere selected
25 from the group consisting of an oxidizing gas atmosphere,

an inert gas atmosphere and a reducing gas atmosphere,
wherein, when the peak intensity ratio of the produced
catalyst and that of the catalyst after a 50 hours reaction
test, which are measured by an extended X-ray absorption
5 fine structure analysis (EXAFS) method, are A(b) and B(b)
respectively, the peak intensity ratios A(b) and B(b)
satisfy the following equation (1):

$$1 \leq B(b)/A(b) \leq 1.45 \quad (1)$$

provided that $A(b) \leq 0.8$,

10 wherein A(b) is a peak intensity ratio of as-produced
Catalyst b measured by the EXAFS method, and B(b) is a peak
intensity ratio of Catalyst b measured by the EXAFS method
after the 50 hours reaction test;
in which

15 50 Hours reaction test: Supported ruthenium oxide
Catalysts a and b are filled in a reactor in this order
from the inlet of the reactor in a weight ratio of 1:10
(Catalyst a to Catalyst b), and a hydrogen chloride gas is
supplied under atmospheric pressure at a flow rate of 0.185
20 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a
flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the
reaction for 50 hours while maintaining the hot spot of
Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, in which Catalyst a is a supported
ruthenium oxide catalyst having a chlorine formation
25 activity per unit mass of the catalyst of 2×10^{-4} to $3 \times$

10⁻⁴ mol/min.g-cat., which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide catalyst produced by the above process,
5 and in which

EXAFS method: Catalyst b is measured by an X-ray absorption fine structure analysis (XAFS) method at the Ru-K absorption edge, and the peak intensity of the catalyst
10 is evaluated by the peak around 0.32 nm in a radial distribution function obtained by the Fourier transformation of the EXAFS spectrum, wherein the peak intensity corresponds to the number of the second nearest neighbor ruthenium atoms of the X-ray absorbing ruthenium
15 atoms in ruthenium dioxide, and the peak intensity ratio of the catalyst is calculated by dividing the peak intensity of the catalyst by that of ruthenium oxide having a particle size of at least 10 nm;

(5) a supported ruthenium oxide catalyst produced by a
20 process comprising the following steps but not a treating step with hydrazine:

supporting a ruthenium compound on a titanium oxide carrier containing the rutile form,
and

25 calcining said supported one at a temperature of 200°C

to 600°C in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere;
and

5 (6) a supported ruthenium oxide catalyst produced by a process comprising the following steps but neither a calcining step nor a treating step with hydrazine:

 supporting a ruthenium halide on a titanium oxide carrier containing the rutile crystal form,

10 and

 drying said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere at a temperature of 20°C to less than 200°C.

15 9. The process according to claim 8, wherein said catalyst (2) is prepared by the process described in (3).

 10. The process according to claim 8, wherein said catalyst is any one of the supported ruthenium oxide catalysts (2), (3) and (4) comprising titanium oxide
20 containing the rutile crystal form as a carrier.

 11. The process according to claim 8, wherein said catalyst is the supported ruthenium oxide catalyst (5), wherein the catalyst is produced by a process comprising the following steps but not a treating step with hydrazine:

25 supporting a ruthenium compound on a carrier,

and

calcining said supported one in an atmosphere selected from the group consisting of an oxidizing gas atmosphere, an inert gas atmosphere and a reducing gas atmosphere, wherein the catalytic activity value of the produced catalyst and the catalytic activity value of the catalyst after 50 hours reaction test , which are measured by a catalytic activity test which is defined below, are respectively C(b) and D(b), and which satisfy the following equation (2):

$$0.79 \leq D(b)/C(b) \leq 1 \quad (2)$$

provided that $C(b) \geq 3.0 \times 10^{-4}$ mol/min.g-cat.

wherein C(b) is a catalytic activity value of the produced catalyst b, which is measured by the catalytic activity test and D(b) is a catalytic activity value of the catalyst b, which is measured by the catalytic activity test after a 50 hours reaction test;

in which

the 50 hours reaction test is carried out by filling supported ruthenium oxide Catalysts a and b in a reactor in this order from the inlet of the reactor in a weight ratio of 1:10 (Catalyst a to Catalyst b), and supplying, under atmospheric pressure, a hydrogen chloride gas at a flow rate of 0.185 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a flow rate of 0.092 to 0.098 mol/g-cat.hr.

to carry out the reaction for 50 hours while maintaining the hot spot of Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, wherein Catalyst a is a catalyst having a chlorine formation activity per unit mass of catalyst of 2×10^{-4} to 3×10^{-4} mol/min.g-cat.,

5 which is obtained in a reaction test for forming chlorine by oxidizing hydrogen chloride with oxygen at 300°C with a molar ratio of hydrogen chloride to oxygen being 1:1, and Catalyst b is a supported ruthenium oxide Catalyst produced by the above process,

10 and in which

Catalytic activity test: 2.3 to 2.5 grams of a catalyst is diluted by mixing with 10 to 20 g of a spherical α -alumina carrier having a diameter of 2 mm, and filled in a quartz reactor tube having an inner diameter of
15 12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric
20 furnace and maintaining the internal temperature (hot spot) at $300 \pm 1^{\circ}\text{C}$, after 2.0 ± 1.0 hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of
25 potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an

iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

5 Chlorine formation activity per unit mass of the catalyst
(mol/min.g-cat.) =
Amount of chlorine gas from reactor exit (mol/min.)/
catalyst weight (g).

12. The process according to claim 8, wherein said
10 catalyst is the supported ruthenium oxide catalyst (6),
wherein the catalyst is produced by a process comprising
the following steps but neither a calcining step nor a
treating step with hydrazine:

supporting a ruthenium halide on a titanium oxide
15 carrier containing the rutile crystal form,
and

drying said supported one in an atmosphere selected
from the group consisting of an oxidizing gas atmosphere,
an inert gas atmosphere and a reducing gas atmosphere at a
20 temperature of 20°C to less than 200°C,
wherein the catalytic activity value of the produced
catalyst and the catalytic activity value of the catalyst
after 50 hours reaction test , which are measured by a
catalytic activity test which is defined below, are
25 respectively E(b) and F(b), and which satisfy the following

equation (3):

$$0.80 \leq F(b)/E(b) \leq 1.20 \quad (3)$$

provided that $E(b) \geq 3.0 \times 10^{-4}$ mol/min.g-cat.

in which

5 50 Hours reaction test: Supported ruthenium oxide
Catalysts a and b are filled in a reactor in this order
from the inlet of the reactor in a weight ratio of 1:10
(Catalyst a to Catalyst b), and a hydrogen chloride gas is
supplied under atmospheric pressure at a flow rate of 0.185
10 to 0.197 mol/g-cat.hr. while supplying an oxygen gas at a
flow rate of 0.092 to 0.098 mol/g-cat.hr. to carry out the
reaction for 50 hours while maintaining the hot spot of
Catalyst b at $360^{\circ}\text{C} \pm 1^{\circ}\text{C}$, in which Catalyst a is a supported
ruthenium oxide catalyst having a chlorine formation
15 activity per unit mass of the catalyst of 2×10^{-4} to $3 \times$
 10^{-4} mol/min.g-cat., which is obtained in a reaction test
for forming chlorine by oxidizing hydrogen chloride with
oxygen at 300°C with a molar ratio of hydrogen chloride to
oxygen being 1:1, and Catalyst b is a supported ruthenium
20 oxide catalyst produced by the above process,
and in which

Catalytic activity test: 2.3 to 2.5 grams of a
catalyst is diluted by mixing with 10 to 20 g of a
spherical α -alumina carrier having a diameter of 2 mm, and
25 filled in a quartz reactor tube having an inner diameter of

12 mm, then a hydrogen chloride gas and an oxygen gas are supplied in the reactor under atmospheric pressure at flow rates of 190 to 210 ml/min. and 190 to 210 ml/min., respectively (both volumes being converted to those at 0°C under 101 kPa) while heating the reactor in an electric furnace and maintaining the internal temperature (hot spot) at $300 \pm 1^\circ\text{C}$, after 2.0 ± 1.0 hours from the start of the reaction, an exit gas from the reactor is sampled by passing it through a 30 mass % aqueous solution of potassium iodide, the amount of formed chlorine and the amount of unreacted hydrogen chloride are measured by an iodine titration method and a neutralization titration method, respectively, and thereafter a chlorine formation activity per unit mass of the catalyst is calculated by the following equation and used as a catalyst activity:

Chlorine formation activity per unit mass of the catalyst (mol/min.g-cat.) =

$$\frac{\text{Amount of chlorine gas from reactor exit (mol/min.)}}{\text{catalyst weight (g)}}$$

ABSTRACT

A supported ruthenium oxide catalyst selected from the group consisting of (1) a supported ruthenium oxide catalyst comprising TiO_2 which contains the rutile crystal form, and which is obtained by calcination at a temperature of at least 550°C , as a carrier; (2) a supported ruthenium oxide catalyst having a carbon monoxide adsorption amount of at least 87.5 ml per one gram of ruthenium contained in the catalyst; (3) a supported ruthenium oxide catalyst obtained by a preparation process comprising the steps of supporting a ruthenium compound on a carrier, calcining the supported one at a temperature of at least 200°C in an oxidizing gas atmosphere, an inert gas atmosphere or a reducing gas atmosphere, treating the calcined one with a mixed solution of hydrazine and an alkaline compound, and oxidizing the hydrazine-treated one. These catalysts have a high catalytic activity and thus produce chlorine in a smaller amount at a lower temperature.